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# Interference Measurements in the Spectra of Neon and Natural Mercury

KEIVIN BURNS,* KENNETH B. ADAMS,** AND JEAN LONGWELL*
*Allegheny Observatory, Pittsburgh, Pennsylvania*
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Accepted neon standards cover the region 6929–5852A. We have observed the first spectrum of neon throughout the region 8919–3126A in order to assist in establishing secondary standards in that part of this range where none exist.

The first spectrum of natural mercury was observed from 7020 to 2200A in order to discover in what part of this range standards of suitable intensity will be available when lines emitted by $Hg^{198}$ have been measured; and to find out which lines (if any) of the natural element may serve as standards when mercury is accidently or unavoidably present in a low pressure source. It is shown that some lines of natural mercury are suitable for secondary standards, and nearly all may be useful when an accuracy of no more than a part per million is required.

THE desirability of having secondary standards of nearly the same wave-length as that of the unknown line has been stressed by all who have engaged in precision spectroscopy. The rare gases afford convenient sources of suitable lines throughout the region 8900–3400A but to date no wave-lengths of these lines have been designated as standards in the regions 8900–7300A and 4200–3300A. Meggers,[1] Humphreys,[2] and these two in collaboration, have made observations of the highest precision in these regions of the rare gas spectra. In order to be accepted as a standard a line should be observed in three laboratories. The Allegheny Observatory and the Westinghouse Research Laboratory present the following table of neon lines which were observed to assist in establishing standards of wave-length shorter and longer than any now accepted in the spectra of the rare gases.

The region 8900–5100A was covered by the Porter spectrograph[3] which has glass lenses of 520-cm focal length. The dispersive agent was a 10-cm glass prism. Two 4×5-in. plates were used in the 10-in. plate holder, 8900–7300A being photographed by the *IN* emulsion, and the red-green region registered on home-dyed plates or on Eastman's "*F*" emulsion. The National Bureau of Standards kindly furnished the glass neon tubes of the Nutting type which were used as sources. The gas pressure was 6 mm or less; the current strength was 20 ma furnished by a 2000-v transformer. Interferometer-plate separations of 6.5, 8, 12, 15, 20, and 40 mm were used, the 40 mm carrying over half the weight. Three pairs of plates were used; glass with rather dense aluminum, fused quartz with lighter aluminum, and crystal quartz with dense silver.

With a large quartz spectrograph (Hilger *E*1) the region 7000–3120A was observed in one adjustment of the instrument. The sources were a quartz Nutting-type tube filled with neon to a pressure of 6 mm, and a similar tube to which a trace of mercury was added intentionally. The latter tube emitted the neon spectrum with about half the brightness of the former and the mercury spectrum in such strength that 5460A of Hg about equaled 5881A of neon in intensity. The relative strength of the two spectra when Ne and Hg are in the same tube depends, of course, on the pressure of neon and on the temperature of the gas. We estimate the quantity of mercury to be in excess of 1 mg/5 cc. By checking against the cadmium standard, both tubes gave the same wave-lengths of the neon lines. In

* Allegheny Observatory
** Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.
[1] W. F. Meggers and C. J. Humphreys, Bur. Stand. J. Research 13, 293 (1934), RP 710.
[2] C. J. Humphreys, J. Research Nat. Bur. Stand. **20**, 24 (1938), RP 1061.
[3] K. Burns and W. F. Meggers, Pub. Allegheny Obs. **6**, 105 (1925). Burns, Meggers, and Kiess, Bur. Stand. J. Research 1, 297 (1928).

TABLE I. Wave-lengths in the spectrum of neon.

| 1 λ A in air | 2 Vacuum wave No. Observed | 3 Comp. | 4 λ *MH*, *H* | 5 ν *M* | 6 Level combinations | 7 No. obs. |
|---|---|---|---|---|---|---|
| 8919.4987 | 11208.318 | 0.317 | | 0.313 | $2p_8 - 3d_8$ | 3 |
| 8865.7562 | 11276.261 | 0.263 | 0.759 | 0.260 | $2p_8 - 3d_4$ | 12 |
| 8865.3057 | 11276.834 | *s* | | 0.82 | $2p_{10} - 2s_3$ | 3 |
| 8853.8669 | 11291.403 | 0.403 | 0.866 | 0.401 | $2p_8 - 3d_3$ | 20 |
| 8830.9078 | 11320.759 | 0.760 | | 0.760 | $2p_8 - 3d_2$ | 2 |
| 8783.7539 | 11381.532 | 0.533 | 0.755 | 0.531 | $2p_2 - 3s_1''$ | 30 |
| 8780.6223 | 11385.592 | 0.594 | 0.6222 | 0.592 | $2p_8 - 3d_1'$ | 34 |
| 8771.6592 | 11397.226 | 0.229 | | 0.229 | $2p_2 - 3s_1'$ | 11 |
| 8704.1132 | 11485.670 | 0.671 | | 0.671 | $2p_7 - 3d_8$ | 6 |
| 8681.9216 | 11515.028 | 0.029 | 0.920 | 0.030 | $2p_7 - 3d_5$ | 15 |
| 8679.4898 | 11518.254 | 0.252 | 0.491 | 0.251 | $2p_3 - 3s_1'$ | 15 |
| 8655.5206 | 11550.151 | 0.149 | | 0.149 | $2p_4 - 3s_1''''$ | 2 |
| 8654.3837 | 11551.668 | 0.668 | 0.3835 | 0.670 | $2p_4 - 3s_1'''$ | 46 |
| 8647.0400 | 11561.479 | 0.477 | | 0.476 | $2p_4 - 3s_1''$ | 8 |
| 8634.6472 | 11578.072 | 0.073 | 0.6480 | 0.072 | $2p_7 - 3d_1''$ | 44 |
| 8591.2583 | 11636.546 | 0.546 | 0.2584 | 0.545 | $2p_4 - 3s_1''''$ | 45 |
| 8571.3535 | 11663.569 | 0.570 | | 0.570 | $2p_8 - 3s_1'$ | 11 |
| 8544.6952 | 11699.957 | 0.957 | | 0.953 | $2p_8 - 3d_6$ | 8 |
| 8495.3591 | 11767.904 | 0.903 | 0.3602 | 0.900 | $2p_8 - 3d_4$ | 56 |
| 8484.4424 | 11783.045 | 0.042 | | 0.041 | $2p_8 - 3d_3$ | 3 |
| 8463.3569 | 11812.400 | 0.400 | | 0.400 | $2p_8 - 3d_2$ | 10 |
| 8418.4265 | 11875.445 | 0.444 | 0.4274 | 0.442 | $2p_8 - 3d_1''$ | 39 |
| 8417.1614 | 11877.230 | 0.234 | | 0.232 | $2p_8 - 3d_1'$ | 1 |
| 8377.6062 | 11933.309 | *d* | 0.6069 | 0.308 | $2p_9 - 3d_4'$ | 57 |
| 8365.7464 | 11950.226 | 0.222 | | 0.222 | $2p_9 - 3d_3$ | 5 |
| 8300.3248 | 12044.415 | 0.414 | 0.3258 | 0.413 | $2p_9 - 3d_1'$ | 48 |
| 8267.1166 | 12092.797 | 0.797 | | 0.796 | $2p_4 - 3s_1''''$ | 2 |
| 8266.0788 | 12094.315 | 0.316 | 0.076 | 0.317 | $2p_4 - 3s_1'''$ | 21 |
| 8259.3795 | 12104.125 | 0.125 | 0.380 | 0.123 | $2p_4 - 3s_1''$ | 11 |
| 8248.6812 | 12119.822 | 0.821 | | 0.821 | $2p_4 - 3s_1'$ | 4 |
| 8136.4061 | 12287.065 | 0.066 | 0.4059 | 0.066 | $2p_7 - 3s_1''''$ | 38 |
| 8128.9077 | 12298.399 | 0.394 | | 0.393 | $2p_7 - 3s_1'''$ | 2 |
| 8118.5495 | 12314.090 | 0.090 | 0.5495 | 0.089 | $2p_7 - 3s_1'$ | 14 |
| 8082.4576 | 12369.078 | 0.077 | 0.4579 | 0.076 | $1s_2 - 2p_{10}$ | 19 |
| 7943.1805 | 12585.958 | 0.956 | 0.1802 | 0.957 | $2p_8 - 3s_1'''$ | 25 |
| 7936.9946 | 12595.767 | 0.765 | | 0.763 | $2p_8 - 3s_1''$ | 5 |
| 7927.1172 | 12611.462 | 0.461 | | 0.461 | $2p_8 - 3s_1'$ | 2 |
| 7839.0550 | 12753.135 | 0.136 | | 0.138 | $2p_9 - 3s_1'''$ | 2 |
| 7724.6281 | 12942.051 | 0.054 | | 0.059 | $2p_1 - 3s_1$ | 2 |
| 7544.0439 | 13251.848 | *d* | 0.046 | 0.844 | $2p_{10} - 3d_8$ | 31 |
| 7535.7739 | 13266.391 | 0.391 | 0.7747 | 0.388 | $2p_{10} - 3d_5$ | 46 |
| 7488.8712 | 13349.476 | 0.476 | 0.8720 | 0.476 | $2p_{10} - 3d_3$ | 48 |
| 7472.4383 | 13378.834 | 0.834 | | 0.835 | $2p_{10} - 3d_2$ | 12 |
| 7438.8981 | 13439.156 | 0.156 | 0.8989 | 0.155 | $1s_3 - 2p_{10}$ | 57 |
| 7245.1665 | 13798.510 | 0.510 | 0.1668 | 0.509 | $1s_4 - 2p_{10}$ | 58 |
| 7173.9380 | 13935.511 | 0.511 | 0.9389 | 0.511 | $1s_5 - 2p_8$ | 54 |
| 7059.1079 | 14162.197 | 0.199 | 0.109 | 0.198 | $2p_{10} - 3s_1''$ | 26 |
| 7051.2937 | 14177.892 | 0.895 | | 0.896 | $2p_{10} - 3s_1'$ | 8 |
| 7032.4128 | 14215.957 | 0.957 | 0.4131 | 0.956 | $1s_5 - 2p_{10}$ | 57 |
| 7024.0500 | 14232.883 | 0.882 | 0.0508 | 0.881 | $1s_2 - 2p_7$ | 44 |
| 6929.4672 | 14427.151 | 0.151 | 0.4679 | 0.151 | $1s_2 - 2p_8$ | 54 |
| 6717.0428 | 14883.402 | 0.402 | | 0.402 | $1s_3 - 2p_8$ | *S* |
| 6678.2764 | 14969.798 | 0.799 | | 0.798 | $1s_5 - 2p_4$ | *S* |
| 6666.8967 | 14995.350 | 0.360 | | 0.365 | $2p_3 - 3s_4$ | 4 |
| 6652.0925 | 15028.722 | 0.720 | | 0.721 | $1s_3 - 2p_3$ | 5 |
| 6598.9529 | 15149.743 | 0.743 | | 0.743 | $1s_3 - 2p_2$ | *S* |
| 6532.8824 | 15302.960 | 0.961 | | 0.960 | $1s_3 - 2p_7$ | *S* |
| 6506.5279 | 15364.943 | 0.944 | | 0.944 | $1s_4 - 2p_8$ | *S* |
| 6444.7118 | 15512.320 | 0.324 | | 0.323 | $2p_8 - 3s_4$ | 7 |
| 6421.7108 | 15567.880 | 0.888 | | 0.896 | $2p_2 - 3s_3$ | 5 |
| 6402.2460 | 15615.211 | 0.211 | | 0.210 | $1s_5 - 2p_9$ | *S* |
| 6382.9914 | 15662.315 | 0.315 | | 0.314 | $1s_4 - 2p_7$ | *S* |
| 6351.8618 | 15739.074 | 0.089 | | 0.093 | $2p_3 - 3s_2$ | 4 |
| 6334.4279 | 15782.391 | 0.391 | | 0.391 | $1s_5 - 2p_5$ | *S* |
| 6328.1646 | 15798.010 | 0.010 | | 0.016 | $2p_4 - 3s_2$ | 7 |
| 6313.6921 | 15834.223 | 0.229 | | 0.237 | $2p_5 - 3s_3$ | 4 |
| 6304.7892 | 15856.582 | 0.584 | | 0.584 | $1s_4 - 2p_6$ | *S* |
| 6293.7447 | 15884.408 | 0.407 | | 0.412 | $2p_5 - 3s_2$ | 7 |
| 6266.4950 | 15953.481 | 0.481 | | 0.481 | $1s_3 - 2p_6$ | *S* |
| 6246.7294 | 16003.960 | 0.964 | | 0.963 | $2p_8 - 3s_5$ | 6 |
| 6217.2813 | 16079.762 | 0.762 | | 0.761 | $1s_5 - 2p_7$ | *S* |
| 6213.8758 | 16088.574 | 0.569 | | 0.575 | $2p_8 - 3s_4$ | 6 |
| 6205.7775 | 16109.569 | 0.569 | | 0.566 | $2p_3 - 4d_2$ | 6 |
| 6193.0663 | 16142.634 | 0.631 | | 0.636 | $2p_4 - 4d_4$ | 4 |
| 6189.0649 | 16153.070 | 0.066 | | 0.067 | $2p_4 - 4d_3$ | 5 |
| 6182.1460 | 16171.148 | 0.144 | 0.146 | 0.144 | $2p_9 - 3s_3$ | 13 |
| 6174.8829 | 16190.169 | 0.172 | | 0.171 | $2p_4 - 4d_1'$ | 5 |
| 6163.5939 | 16219.823 | 0.822 | | 0.822 | $1s_3 - 2p_5$ | *S* |
| 6143.0623 | 16274.032 | 0.031 | | 0.031 | $1s_5 - 2p_6$ | *S* |
| 6128.4498 | 16312.835 | 0.835 | 0.4510 | 0.835 | $1s_4 - 2p_5$ | 18 |
| 6096.1630 | 16399.232 | 0.232 | | 0.231 | $1s_4 - 2p_4$ | *S* |
| 6074.3377 | 16458.153 | 0.153 | | 0.154 | $1s_4 - 2p_3$ | *S* |
| 6064.5359 | 16484.754 | 0.749 | | 0.757 | $2p_7 - 3s_2$ | 6 |
| 6046.1348 | 16534.924 | 0.927 | | 0.933 | $2p_7 - 3s_3$ | 5 |
| 6029.9971 | 16579.175 | 0.176 | | 0.176 | $1s_4 - 2p_2$ | *S* |
| 6000.9275 | 16659.486 | 0.490 | | 0.500 | $2p_8 - 4d_5$ | 6 |
| 5991.6532 | 16685.273 | 0.279 | | 0.283 | $2p_8 - 4d_4$ | 8 |
| 5987.9074 | 16695.711 | 0.714 | 0.9069 | 0.714 | $2p_8 - 4d_3$ | 10 |
| 5975.5340 | 16730.282 | 0.282 | | 0.282 | $1s_5 - 2p_5$ | *S* |
| 5974.6273 | 16732.821 | 0.820 | 0.628 | 0.818 | $2p_8 - 4d_1'$ | 3 |
| 5965.4710 | 16758.504 | 0.503 | 0.474 | 0.501 | $2p_2 - 4s_1''$ | 13 |
| 5961.6228 | 16769.322 | 0.320 | | 0.309 | $2p_2 - 4s_1'$ | 7 |
| 5944.8342 | 16816.679 | 0.679 | | 0.678 | $1s_5 - 2p_4$ | *S* |
| 5918.9068 | 16890.342 | 0.343 | | 0.331 | $2p_3 - 4s_1'$ | 8 |
| 5913.6327 | 16905.406 | 0.407 | 0.633 | 0.406 | $2p_7 - 4d_5$ | 10 |
| 5906.4294 | 16926.023 | 0.026 | 0.429 | 0.029 | $2p_7 - 4d_1''$ | 12 |
| 5902.7835 | 16936.478 | 0.470 | | 0.471 | $2p_4 - 4s_1''''$ | 2 |
| 5902.4623 | 16937.399 | 0.401 | 0.464 | 0.397 | $2p_4 - 4s_1'''$ | 20 |

TABLE I (*continued*).

| 1 λ A in air | 2 Vacuum wave No. Observed | 3 Comp. | 4 λ *MH*, *H* | 5 ν *M* | 6 Level combinations | 7 No. obs. |
|---|---|---|---|---|---|---|
| 5881.8950 | 16996.624 | 0.623 | | 0.623 | $1s_5 - 2p_3$ | *S* |
| 5872.8275 | 17022.867 | 0.867 | 0.828 | 0.867 | $2p_8 - 4s_1''''$ | 12 |
| 5868.4183 | 17035.657 | 0.661 | | 0.650 | $2p_8 - 4s_1'$ | 4 |
| 5852.4878 | 17082.026 | 0.026 | | 0.027 | $1s_2 - 2p_1$ | *S* |
| 5820.1558 | 17176.920 | 0.919 | 0.1550 | 0.923 | $2p_8 - 4d_4$ | 44 |
| 5811.4066 | 17202.780 | 0.778 | | 0.776 | $2p_8 - 4d_3$ | 5 |
| 5804.4496 | 17223.399 | 0.397 | 0.4488 | 0.399 | $2p_8 - 4d_1''$ | 25 |
| 5764.4188 | 17343.004 | *d* | 0.418 | 0.007 | $2p_9 - 4d_4'$ | 55 |
| 5760.5885 | 17354.536 | 0.534 | | 0.535 | $2p_9 - 4d_3$ | 4 |
| 5748.2985 | 17391.640 | 0.640 | 0.299 | 0.639 | $2p_9 - 4d_1'$ | 30 |
| 5719.2248 | 17480.049 | 0.049 | 0.2254 | 0.044 | $2p_4 - 4s_1'''$ | 17 |
| 5689.8163 | 17570.397 | 0.398 | 0.8164 | 0.398 | $2p_{10} - 3s_3$ | 24 |
| 5662.5489 | 17655.005 | 0.003 | 0.547 | 0.010 | $2p_{10} - 3s_2$ | 9 |
| 5656.6588 | 17673.387 | 0.387 | 0.6585 | 0.388 | $2p_7 - 4s_1''''$ | 25 |
| 5652.5664 | 17686.182 | 0.181 | | 0.171 | $2p_7 - 4s_1'$ | 7 |
| 5562.7662 | 17971.690 | 0.689 | 0.769 | 0.684 | $2p_8 - 4s_1'''$ | 21 |
| 5538.6510 | 18049.939 | 0.932 | | 0.937 | $2p_3 - 4s_4$ | 1 |
| 5533.6788 | 18066.155 | 0.156 | | 0.158 | $2p_4 - 4s_3$ | 2 |
| 5494.4158 | 18195.256 | 0.250 | | 0.256 | $2p_8 - 4s_4$ | 2 |
| 5448.5091 | 18348.559 | 0.554 | 0.508 | 0.563 | $2p_{10} - 3s_3$ | 5 |
| 5433.6513 | 18398.731 | 0.732 | 0.649 | 0.738 | $2p_{10} - 3s_2$ | 9 |
| 5418.5584 | 18449.977 | 0.969 | | 0.001 | $2p_2 - 5d_5$ | 2 |
| 5412.6490 | 18470.121 | 0.123 | | 0.127 | $2p_2 - 5d_3$ | 1 |
| 5400.5616 | 18511.460 | 0.459 | 0.5620 | 0.460 | $1s_4 - 2p_1$ | 46 |
| 5383.2503 | 18570.989 | 0.992 | | 1.023 | $2p_3 - 5d_5$ | 1 |
| 5374.9774 | 18599.572 | 0.572 | 0.975 | 0.586 | $2p_3 - 5d_3$ | 2 |
| 5372.3110 | 18608.802 | 0.804 | | 0.805 | $2p_8 - 4s_3$ | 6 |
| 5360.0121 | 18651.501 | 0.501 | 0.012 | 0.507 | $2p_8 - 4s_4$ | 4 |
| 5349.2038 | 18689.187 | 0.194 | | 0.189 | $2p_2 - 4s_2$ | 2 |
| 5343.2834 | 18709.895 | *d* | 0.284 | 0.893 | $2p_{10} - 4d_8$ | 16 |
| 5341.0938 | 18717.565 | 0.564 | 0.092 | 0.575 | $2p_{10} - 4d_5$ | 22 |
| 5330.7775 | 18753.788 | 0.788 | 0.7766 | 0.789 | $2p_{10} - 4d_3$ | 28 |
| 5326.3968 | 18769.212 | 0.212 | 0.396 | 0.211 | $2p_{10} - 4d_2$ | 8 |
| 5304.7580 | 18845.772 | 0.770 | 0.756 | 0.777 | $2p_7 - 4s_4$ | 5 |
| 5298.1891 | 18869.138 | 0.138 | 0.190 | 0.134 | $2p_4 - 4s_2$ | 9 |
| 5280.0853 | 18933.834 | 0.829 | | 0.827 | $2p_5 - 4s_3$ | 4 |
| 5274.0393 | 18955.539 | 0.535 | | 0.530 | $2p_5 - 4s_2$ | 1 |
| 5234.0271 | 19100.446 | 0.444 | 0.028 | 0.445 | $2p_3 - 4s_3$ | 5 |
| 5222.3517 | 19143.146 | 0.141 | 0.351 | 0.147 | $2p_3 - 4s_4$ | 10 |
| 5214.3389 | 19172.563 | 0.561 | | 0.593 | $2p_4 - 5d_5$ | 1 |
| 5210.5672 | 19186.441 | 0.438 | 0.573 | 0.437 | $2p_6 - 5d_4$ | 2 |
| 5208.8648 | 19192.712 | 0.715 | 0.863 | 0.719 | $2p_6 - 5d_3$ | 7 |
| 5203.8962 | 19211.037 | 0.036 | 0.8950 | 0.041 | $2p_6 - 5d_1'$ | 15 |
| 5193.2227 | 19250.520 | 0.520 | 0.224 | 0.521 | $2p_2 - 5s_1''$ | 2 |
| 5193.1302 | 19250.863 | 0.881 | 0.130 | 0.878 | $2p_2 - 5s_1''''$ | 2 |
| 5191.3223 | 19257.568 | 0.566 | | 0.57 | $2p_2 - 5s_1'$ | 1 |
| 5188.6122 | 19267.626 | 0.624 | 0.612 | 0.626 | $2p_9 - 4s_2$ | 14 |
| 5158.9018 | 19378.588 | 0.589 | | 0.59 | $2p_3 - 5s_1'$ | 2 |
| 5156.6672 | 19386.985 | 0.984 | 0.664 | 0.989 | $2p_7 - 5d_3$ | 1 |
| 5154.4271 | 19395.410 | 0.410 | 0.422 | 0.426 | $2p_7 - 5d_2$ | 3 |
| 5151.9610 | 19404.695 | 0.692 | 0.963 | 0.690 | $2p_7 - 5d_1''$ | 8 |
| 5144.9384 | 19431.181 | 0.182 | 0.9376 | 0.182 | $2p_4 - 5s_1'''$ | 12 |
| 5122.2565 | 19517.223 | 0.222 | 0.257 | 0.219 | $2p_5 - 5s_1''''$ | 9 |
| 5116.5032 | 19539.169 | 0.169 | 0.503 | 0.168 | $2p_{10} - 4s_1''$ | 20 |
| 5113.6724 | 19549.985 | 0.986 | 0.675 | 0.976 | $2p_{10} - 4s_1'$ | 7 |
| 5104.7011 | 19584.344 | 0.349 | 0.705 | 0.348 | $2p_7 - 4s_3$ | 3 |
| 5080.3852 | 19678.077 | 0.078 | 0.383 | 0.077 | $2p_8 - 5d_4$ | 13 |
| 5074.2007 | 19702.061 | 0.063 | 0.200 | 0.060 | $2p_8 - 5d_1''$ | 8 |
| 5037.7512 | 19844.608 | *d* | 0.7505 | 0.612 | $2p_9 - 5d_4'$ | 19 |
| 5031.3504 | 19869.854 | 0.856 | 0.3484 | 0.862 | $2p_9 - 5d_1'$ | 8 |
| 5022.864 *c* | 19903. | 0.426 | 0.870 | 0.421 | $2p_8 - 4s_2$ | *c* |
| 5011. | 19950. | | 0.003 | 0.536 | $2p_3 - 6d_2$ | |
| 5005.1587 | 19973.832 | 0.830 | 0.160 | 0.829 | $2p_8 - 5s_1'''$ | 5 |
| 4994.913 *c* | 20014. | 0.727 | 0.930 | 0.748 | $2p_4 - 6d_1'$ | *c* |
| 4957.123 *c* | 20167. | 0.381 | 0.122 | 0.383 | $2p_7 - 5s_1''$ | *c* |
| 4957.0335 | 20167.743 | 0.742 | 0.0334 | 0.740 | $2p_7 - 5s_1''''$ | 5 |
| 4944.9899 | 20216.848 | 0.873 | 0.987 | 0.863 | $2p_8 - 5s_4$ | 1 |
| 4939.0457 | 20241.194 | 0.195 | 0.041 | 0.211 | $2p_8 - 5s_4$ | 1 |
| 4928.241 *c* | 20285. | 0.570 | 0.235 | 0.584 | $2p_3 - 5s_2$ | *c* |
| 4892.1007 | 20435.428 | 0.468 | 0.090 | 0.481 | $2p_7 - 5s_4$ | 1 |
| 4884.9170 | 20465.480 | 0.470 | 0.915 | 0.469 | $2p_8 - 5s_1'''$ | 5 |
| 4866.477 *c* | 20543. | 0.026 | 0.476 | 0.029 | $2p_8 - 6d_4$ | *c* |
| 4865.5009 | 20547.147 | 0.141 | 0.505 | 0.138 | $2p_8 - 6d_3$ | 1 |
| 4863.0800 | 20557.375 | 0.375 | 0.074 | 0.395 | $2p_8 - 6d_1'$ | 4 |
| 4852.6571 | 20601.530 | 0.527 | 0.655 | 0.538 | $2p_2 - 6s_1''$ | 2 |
| 4837.3139 | 20666.873 | 0.878 | 0.3118 | 0.880 | $2p_{10} - 4s_4$ | 7 |
| 4827.587 *c* | 20708. | 0.513 | 0.587 | 0.513 | $2p_8 - 5s_4$ | *c* |
| 4827.3444 | 20709.554 | 0.575 | 0.338 | 0.582 | $2p_{10} - 4s_4$ | 3 |
| 4821.9236 | 20732.836 | 0.835 | 0.924 | 0.851 | $2p_8 - 5s_4$ | 2 |
| 4817.6386 | 20751.276 | 0.275 | 0.636 | 0.289 | $2p_7 - 6d_1''$ | 2 |
| 4810.0640 | 20783.954 | 0.954 | 0.0625 | 0.966 | $2p_4 - 6s_1'''$ | 7 |
| 4800.100 *c* | 20827. | 0.094 | 0.111 | 0.050 | $2p_4 - 7d_1'$ | *c* |
| 4790.217 *c* | 20870. | 0.067 | 0.218 | 0.067 | $2p_8 - 6s_1''''$ | *c* |
| 4788.9270 | 20875.687 | 0.693 | 0.9258 | 0.694 | $2p_9 - 5s_3$ | 3 |
| 4780. | 20913. | | 0.338 | 0.196 | $2p_8 - 7d_1''$ | |
| 4758.726 *c* | 21008. | 0.162 | 0.728 | 0.176 | $2p_6 - 5s_2$ | *c* |
| 4752.7320 | 21034.666 | *d* | 0.7313 | 0.669 | $2p_3 - 6d_4$ | 7 |
| 4749.5754 | 21048.646 | 0.646 | 0.572 | 0.659 | $2p_3 - 6d_1''$ | 3 |
| 4725. | 21157. | | 0.145 | 0.474 | $2p_4 - 6s_4$ | |
| 4715.3466 | 21201.436 | *d* | 0.344 | 0.447 | $2p_9 - 6d_4'$ | 9 |
| 4712.0661 | 21216.196 | 0.195 | | 0.216 | $2p_9 - 6d_1'$ | 1 |
| 4710.0669 | 21225.202 | *d* | | 0.23 | $2p_{10} - 5d_4$ | 3 |
| 4708.8619 | 21230.633 | 0.635 | 0.854 | 0.668 | $2p_{10} - 5d_3$ | 5 |
| 4704.3949 | 21250.790 | 0.789 | 0.395 | 0.794 | $2p_{10} - 5d_2$ | 13 |
| 4687.6724 | 21326.600 | 0.602 | 0.671 | 0.613 | $2p_4 - 6s_1'''$ | 1 |
| 4679. | 21365. | | 0.135 | 0.510 | $2p_8 - 7d_2$ | |
| 4678. | 21369. | 0.742 | 0.218 | 0.697 | $2p_8 - 7d_1'$ | |
| 4670. | 21403. | | 0.884 | 0.252 | $2p_4 - 6s_2$ | |

TABLE I (*continued*).

| 1 λ A in air | 2 Vacuum wave No. Observed | 3 Comp. | 4 λ *MH*, *H* | 5 ν *M* | 6 Level combinations | 7 No obs. |
|---|---|---|---|---|---|---|
| 4661.1054 | 21448.153 | 0.154 | 0.104 | 0.153 | $2p_{10}-4s_2$ | 4 |
| 4656.3936 | 21469.856 | 0.860 | 0.3923 | 0.856 | $2p_{10}-4s_2$ | 5 |
| 4649. | 21499. | 0.802 | 0.904 | 0.816 | $2p_8-5s_2$ | |
| 4645.4180 | 21520.587 | *s* | 0.416 | 0.588 | $2p_7-6s_1''''$ | 4 |
| 4636. | 21563. | | 0.125 | 0.717 | $2p_7-7d_1''$ | |
| 4628.3113 | 21600.122 | *s* | 0.309 | 0.134 | $2p_4-7s_1'''$ | 1 |
| 4617. | 21649. | | 0.837 | 0.114 | $2p_8-6s_4$ | |
| 4614. | 21665. | | 0.391 | 0.283 | $2p_8-6s_4$ | |
| 4609. | 21686. | | 0.910 | 0.335 | $2p_5-7s_1''''$ | |
| 4582.4521 | 21816.285 | *s* | 0.450 | 0.294 | $2p_9-6s_3$ | 4 |
| 4582. | 21817. | 0.958 | 0.035 | 0.958 | $2p_8-6s_1''''$ | |
| 4575.0620 | 21851.522 | *d* | 0.060 | 0.533 | $2p_8-7d_4$ | 2 |
| 4573. | | | 0.759 | | | |
| 4565. | 21895. | | 0.888 | 0.428 | $2p_6-8d_1'$ | |
| 4552. | 21959. | | 0.598 | 0.344 | $2p_7-7s_4$ | |
| 4540.3801 | 22018.434 | *d* | 0.376 | 0.455 | $2p_9-7d_4'$ | 3 |
| 4538.2927 | 22028.562 | *d* | | 0.518 | $2p_9-7d_3'$ | 1 |
| 4537.7545 | 22031.174 | 0.186 | 0.751 | 0.188 | $2p_{10}-5s_1''$ | 1 |
| 4525. | 22089. | | 0.764 | 0.543 | $2p_7-8d_1''$ | |
| 4517. | 22128. | | 0.736 | 0.795 | $2p_4-8s_1'''$ | |
| 4500. | 22214. | | 0.182 | 0.99 | $2p_5-8s_1''$ | |
| 4488.0926 | 22274.953 | 0.947 | 0.0928 | 0.948 | $2p_{10}-5s_4$ | 5 |
| 4483.199 *c* | 22299. | 0.269 | 0.190 | 0.286 | $2p_{10}-5s_4$ | *c* |
| 4475. | 22336. | | 0.656 | 0.856 | $2p_7-7s_1''''$ | |
| 4466.8120 | 22381.072 | *d* | 0.807 | 0.097 | $2p_9-8d_4$ | 1 |
| 4460. | 22414. | | 0.175 | 0.375 | $2p_9-7s_4$ | 1 |
| 4433.7239 | 22548.096 | *d* | 0.721 | 0.110 | $2p_9-8d_3'$ | 1 |
| 4425. | 22590. | | 0.400 | 0.506 | $2p_{10}-6d_5$ | |
| 4424.8096 | 22593.519 | *d* | 0.800 | 0.569 | $2p_{10}-6d_5$ | 4 |
| 4422.5205 | 22605.213 | 0.215 | 0.519 | 0.213 | $2p_{10}-6d_3$ | 3 |
| 4395. | 22743. | | 0.556 | 0.883 | $2p_8-9d_4$ | |
| 4381. | 22818. | | 0.220 | 0.303 | $2p_9-8s_4$ | |
| 4363. | 22910. | | 0.524 | 0.840 | $2p_9-9d_3'$ | |
| 4334.1267 | 23066.236 | *s* | 0.125 | 0.251 | $2p_{10}-5s_2$ | 1 |
| 4306.2625 | 23215.487 | | | 0.549 | $2p_{10}-6s_2$ | 1 |
| 4275.5598 | 23382.192 | 0.193 | | 0.205 | $2p_{10}-6s_1''$ | 5 |
| 4270.2674 | 23411.173 | *d* | | 0.39 | $2p_{10}-7d_5$ | 4 |
| 3754.2148 | 26629.188 | 0.184 | 0.2160 | 0.180 | $1s_2-3p_{10}$ | 13 |
| 3701.2247 | 27010.427 | 0.427 | 0.2250 | 0.423 | $1s_2-3p_8$ | 23 |
| 3685.7351 | 27123.938 | 0.938 | 0.7359 | 0.930 | $1s_2-3p_7$ | 23 |
| 3682.2421 | 27149.665 | 0.667 | 0.2428 | 0.660 | $1s_2-3p_6$ | 20 |
| 3633.6643 | 27512.613 | 0.617 | 0.6646 | 0.611 | $1s_2-3p_3$ | 23 |
| 3609.1787 | 27699.263 | 0.263 | 0.1793 | 0.259 | $1s_2-3p_{10}$ | 9 |
| 3600.1694 | 27768.577 | 0.581 | 0.1693 | 0.578 | $1s_2-3p_9$ | 26 |
| 3593.639 *c* | 27819. | 0.036 | 0.6398 | 0.029 | $1s_2-3p_2$ | *c* |
| 3593.5263 | 27819.910 | 0.912 | 0.5259 | 0.911 | $1s_2-3p_4$ | 21 |
| 3562.9551 | 28058.605 | 0.617 | | 0.613 | $1s_4-3p_{10}$ | 6 |
| 3520.4714 | 28397.197 | *p* | 0.4717 | 0.194 | $1s_2-3p_1$ | 37 |
| 3515.1900 | 28439.862 | 0.860 | 0.1908 | 0.856 | $1s_4-3p_8$ | 31 |
| 3510.7207 | 28476.065 | 0.064 | 0.7214 | 0.060 | $1s_5-3p_{10}$ | 24 |
| 3501.2154 | 28553.370 | 0.371 | 0.2165 | 0.363 | $1s_4-3p_7$ | 29 |
| 3498.0632 | 28579.101 | 0.100 | 0.0644 | 0.093 | $1s_4-3p_6$ | 28 |
| 3472.5706 | 28788.898 | *p* | 0.5711 | 0.893 | $1s_5-3p_9$ | 34 |
| 3466.5781 | 28838.664 | 0.662 | 0.5786 | 0.657 | $1s_3-3p_5$ | 28 |
| 3464.3385 | 28857.304 | 0.307 | 0.3389 | 0.303 | $1s_5-3p_8$ | 28 |
| 3460.5235 | 28889.117 | 0.115 | 0.5245 | 0.108 | $1s_3-3p_2$ | 31 |
| 3454.1942 | 28942.053 | 0.050 | 0.1952 | 0.044 | $1s_4-3p_3$ | 35 |
| 3450.7641 | 28970.818 | 0.818 | 0.7653 | 0.810 | $1s_5-3p_7$ | 30 |
| 3447.7022 | 28996.547 | 0.547 | 0.7029 | 0.540 | $1s_5-3p_6$ | 38 |
| 3423.9120 | 29198.017 | 0.014 | 0.9127 | 0.011 | $1s_4-3p_5$ | 17 |
| 3418. | 29248. | 0.469 | 0.0066 | 0.462 | $1s_4-3p_2$ | |
| 3417.9031 | 29249.346 | 0.345 | 0.9036 | 0.344 | $1s_4-3p_4$ | 31 |
| 3375.6489 | 29615.459 | 0.461 | 0.6498 | 0.458 | $1s_5-3p_5$ | 10 |
| 3369.9069 | 29665.920 | 0.916 | 0.9081 | 0.909 | $1s_5-3p_2$ | 25 |
| 3369.8076 | 29666.795 | 0.792 | 0.8086 | 0.791 | $1s_5-3p_4$ | 1 |
| 3167.5762 | 31560.778 | *p* | | 0.77 | $1s_2-4p_{10}$ | 4 |
| 3153.4107 | 31702.547 | *p* | | 0.51 | $1s_2-4p_8$ | 4 |
| 3148.6107 | 31750.873 | *p* | | 0.86 | $1s_2-4p_7$ | 5 |
| 3126.1986 | 31978.490 | *p* | | 0.50 | $1s_2-4p_3$ | 3 |

addition to the interferometer plates used for the long waves, a pair of crystal-quartz plates coated lightly with aluminum was employed, and separations of 2, 3.75, 5, and 25 mm in addition to those aforementioned.

In Table I the first and second columns contain, respectively, the measured wave-lengths in standard air and the corresponding wave numbers in vacuum.[4] The third column shows the fractional part of the differences of the levels of column six. A letter in this column indicates that this level was found only once. These levels have been adjusted so that agreement between observed and computed is best for lines of greatest weight. The fourth column contains the fractional wave-length as measured by Meggers and Humphreys[1] (8865–4334A), or by Humphreys[2] (3754–3369A). Column five contains the fractional differences of levels as published by Charlotte Moore,[5] "compiled from an unpublished manuscript kindly furnished by Edlén." Column seven shows the number of observations. An "*S*" in this column indicates that the wavelength is that recommended by The International Astronomical Union[6] and the wave number in column two corresponds to this value.

In setting up the levels, $1s_4$ was adopted as given by Charlotte Moore.[5] The difference $1s_5$–$1s_4$ occurs in nine well-observed line pairs; the mean of these nine values was applied to $1s_4$ to obtain $1s_5$. Similarly, $1s_3$ was derived from five pairs and $1s_2$ from fifteen. In setting up the $p$ levels, it was seen that the level $1s_3$ was systematically 0.002 too low, the result of including one discordant observation in comparing this level with $1s_4$. The $p$ levels were derived from combinations with the $1s$ levels. The $2s$ and all higher odd levels were found from combinations with the $2p$ group. An asterisk indicates that the level was found in only one combination. The level $2p_9$ was derived from only one pair-difference, both lines being standards. This level is checked against other $2p$ levels but the accuracy of the other combinations is not great enough to add much weight to the single difference here used.

In the region of wave-lengths longer than the standards, 8865–6929A, the mean difference $AOW-MH$ is −0.0005A; the median difference is 0.0005A, a part in sixteen million. In the region of the standards, 6717–5852A, for lines other than the standards the difference $AOW-MH$ is −0.0006A. From 5820 to 5100A we used both the glass and the quartz spectrographs; here the well-observed lines show the negligible systematic difference +0.0004A between results from the two laboratories. From 5100 to 4300A, the end of the $MH$ table, $AOW-MH=+0.0010$A. In the region measured by Humphreys, 3754–3369A, the difference $AOW-H$ is −0.0007A; after applying this systematic difference the largest $AOW-H$ is 0.0005A, the median is 0.0003A. The presence of these discrepancies suggests an examination of the manner in which the correction for phase was derived. We assume that the wave-length determined from the thickest interferometer is most nearly free of error and that the error is inversely proportional to the order number. On these assumptions the correction applicable to a thickness of 20 mm for the crystal quartz thinly aluminized is −0.0012A from 3750 to 3360A; for the fused quartz plates with medium coat of aluminum the correction is zero at the beginning and +0.0002A at the end of this range; for the crystal quartz with heavy silver the correction is zero at 3750A

[4] W. F. Meggers and C. G. Peters, Sci. Papers Bur. Stand. **14**, 697 (1918), SP 327.

[5] C. Moore, "Atomic energy levels. Vol. I," Circ. Nat. Bur. Stand. **467**, 76 (1949).

[6] Trans. Int. Astr. Union **5**, 86 (1935).

and +0.0012A at 3360A; the glass plates with heavy aluminum have correction zero throughout the range.

Between 3400 and 2300A where all rare gas spectra are weak the mercury spectrum has several lines strong enough to serve as standards; many of these lines, especially the strongest at 2536A, are complex and not to be recommended when natural mercury is the source. For this region, in fact throughout the whole range 5790–2300A, the perfect source of standards has been introduced by Meggers[7] whose efforts have resulted in making the use of $Hg^{198}$ practical. It would be difficult to overestimate the benefits which the availability of a single even-numbered isotope of mercury will bring to precision spectroscopy. Wherever a line of sufficient strength is emitted by this source there is no point in looking for any other standard. Consequently we have examined the mercury spectrum from 7000 to 2100A to locate the lines which are of sufficient strength when the source is the neon-mercury tube mentioned earlier. By using interferometer films of moderate density under the observing conditions described above, the exposure time necessary to register a mercury line is: One second or less for 4358 and 2536A; five to ten seconds for 5460, 4046, 3650, 3341, 3131, and 3125A (and Ne 5881A); one minute for 3021 and 2967A; two minutes for 2893, 2803, and 2652A (four minutes for Ne 5400A); ten minutes for 2464, 2446, 2399, and 2378A. These figures give only a rough indication of the required exposure time since mercury lines of sufficient sharpness may be obtained at intensities which vary by a factor of ten as the temperature of the tube and the current strength are changed.

Mercury shows no strong red lines; here neon and cadmium are already available. Between 3261 and 2141A cadmium has some possible standards which are stronger than the mercury lines of this region with the

TABLE II. Neon I levels.

| J | | AOW | CM | J | | AOW | CM | J | | AOW | CM |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Even | | | | | |
| 1 | $2p_{10}$ | 48259.747 | 0.746 | 1 | $3p_{10}$ | 62519.854 | 0.850 | 1 | $4p_{10}$ | 67451.448* | 0.44 |
| 3 | $2p_9$ | 49659.001* | 0.000 | 3 | $3p_9$ | 62832.688* | 0.683 | 3 | $4p_9$ | 67561. | 0.03 |
| 2 | $2p_8$ | 49826.181 | 0.181 | 2 | $3p_8$ | 62901.097 | 0.093 | 2 | $4p_8$ | 67593.217* | 0.18 |
| 1 | $2p_7$ | 50123.552 | 0.551 | 1 | $3p_7$ | 63014.608 | 0.600 | 1 | $4p_7$ | 67641.543* | 0.53 |
| 2 | $2p_6$ | 50317.821 | 0.821 | 2 | $3p_6$ | 63040.337 | 0.330 | 2 | $4p_6$ | 67650. | 0.60 |
| 1 | $2p_5$ | 50774.072 | 0.072 | 1 | $3p_5$ | 63659.251 | 0.248 | 1 | $4p_5$ | 68357. | 0.44 |
| 2 | $2p_4$ | 50860.469 | 0.468 | 2 | $3p_4$ | 63710.582 | 0.581 | 2 | $4p_4$ | 68380. | 0.69 |
| 0 | $2p_3$ | 50919.390 | 0.391 | 0 | $3p_3$ | 63403.287 | 0.281 | 0 | $4p_3$ | 67869.160* | 0.17 |
| 1 | $2p_2$ | 51040.413 | 0.413 | 1 | $3p_2$ | 63709.706 | 0.699 | 1 | $4p_2$ | 68360. | 0.57 |
| 0 | $2p_1$ | 52972.696 | 0.697 | 0 | $3p_1$ | 64287.867* | 0.864 | 0 | $4p_1$ | 68588. | 0.83 |
| | | | | | | Odd | | | | | |
| 2 | $1s_5$ | 34043.790 | 0.790 | 2 | $2s_5$ | 58603. | 0.070 | 2 | $3s_1''''$ | 62410.618 | 0.617 |
| 1 | $1s_4$ | 34461.237 | 0.237 | 1 | $2s_4$ | 58797 | 0.954 | 3 | $3s_1'''$ | 62412.137 | 0.138 |
| 0 | $1s_3$ | 34820.589 | 0.591 | 0 | $2s_3$ | 59381. | 0.94 | 2 | $3s_1''$ | 62421.946 | 0.944 |
| 1 | $1s_2$ | 35890.670 | 0.670 | 1 | $2s_2$ | 59536.581* | 0.57 | 1 | $3s_1'$ | 62437.642 | 0.642 |
| 2 | $3s_5$ | 65830.145 | 0.144 | 2 | $4s_1''''$ | 67796.939 | 0.939 | 2 | $4s_5$ | 68926.625 | 0.626 |
| 1 | $3s_4$ | 65914.750 | 0.756 | 3 | $4s_1'''$ | 67797.870 | 0.865 | 1 | $4s_4$ | 68969.322 | 0.328 |
| 0 | $3s_3$ | 66608.301 | 0.309 | 2 | $4s_1''$ | 67798.916 | 0.914 | 0 | $4s_3$ | 69707.901 | 0.899 |
| 1 | $3s_2$ | 66658.479 | 0.484 | 1 | $4s_1'$ | 67809.733 | 0.722 | 1 | $4s_2$ | 69729.607 | 0.602 |
| 2 | $5s_1''''$ | 70291.294 | 0.291 | 2 | $5s_5$ | 70534.694 | 0.694 | 2 | $6s_1''''$ | 71644.139* | 0.139 |
| 3 | $5s_1'''$ | 70291.651 | 0.650 | 1 | $5s_4$ | 70559.016 | 0.032 | 3 | $6s_1'''$ | 71644.423 | 0.434 |
| 2 | $5s_1''$ | 70290.933* | 0.934 | 0 | $5s_3$ | 71314. | 0.84 | 2 | $6s_1''$ | 71641.940 | 0.951 |
| 1 | $5s_1'$ | 70297.979 | 0.98 | 1 | $5s_2$ | 71325.983* | 0.997 | 1 | $6s_1'$ | 71646. | 0.87 |
| 0 | $3d_6$ | 61511.595* | 0.590 | 0 | $4d_6$ | 66969.642* | 0.639 | 0 | $5d_6$ | 69484.949* | 0.98 |
| 1 | $3d_5$ | 61526.138 | 0.134 | 1 | $4d_5$ | 66977.311 | 0.321 | 1 | $5d_5$ | 69490.382 | 0.414 |
| 4 | $3d_4'$ | 61592.310* | 0.308 | 4 | $4d_4'$ | 67002.005* | 0.007 | 4 | $5d_4'$ | 69503.609* | 0.612 |
| 3 | $3d_4$ | 61594.084 | 0.081 | 3 | $4d_4$ | 67003.100 | 0.104 | 3 | $5d_4$ | 69504.259 | 0.258 |
| 2 | $3d_3$ | 61609.223 | 0.222 | 2 | $4d_3$ | 67013.535 | 0.535 | 2 | $5d_3$ | 69510.536 | 0.540 |
| 1 | $3d_2$ | 61638.581 | 0.581 | 1 | $4d_2$ | 67028.959 | 0.957 | 1 | $5d_2$ | 69518.962 | 0.977 |
| 2 | $3d_1''$ | 61701.625 | 0.623 | 2 | $4d_1''$ | 67049.578 | 0.580 | 2 | $5d_1''$ | 69528.244 | 0.241 |
| 3 | $3d_1'$ | 61703.415 | 0.413 | 3 | $4d_1'$ | 67050.641 | 0.639 | 3 | $5d_1'$ | 69528.857 | 0.862 |
| 0 | $6d_6$ | 70850. | 0.252 | 0 | $7d_6$ | 71671. | 0.14 | 0 | $8d_6$ | 72202. | 0.33 |
| 1 | $6d_5$ | 70853.266* | 0.315 | 1 | $7d_5$ | 71673. | 0.90 | 1 | $8d_5$ | 72203. | 0.86 |
| 4 | $6d_4'$ | 70860.437* | 0.447 | 4 | $7d_4'$ | 71677.435* | 0.455 | 4 | $8d_4'$ | 72207.097* | 0.110 |
| 3 | $6d_4$ | 70860.847 | 0.850 | 3 | $7d_4$ | 71677.703* | 0.714 | 3 | $8d_4$ | 72207.253* | 0.278 |
| 2 | $6d_3$ | 70864.962 | 0.959 | 2 | $7d_3$ | 71683. | 0.331 | 2 | $8d_3$ | 72208. | 0.77 |
| 1 | $6d_2$ | 70869. | 0.927 | 1 | $7d_2$ | 71684. | 0.902 | 1 | $8d_2$ | 72211. | 0.10 |
| 2 | $6d_1''$ | 70874.827 | 0.840 | 2 | $7d_1''$ | 71687. | 0.268 | 2 | $8d_1''$ | 72213. | 0.094 |
| 3 | $6d_1'$ | 70875.196 | 0.216 | 3 | $7d_1'$ | 71687. | 0.518 | 3 | $8d_1'$ | 72213. | 0.249 |

* No check.

[7] W. F. Meggers, J. Opt. Soc. Am. **38**, 7 (1948).

exception of 2536A. Our measurements of the cadmium lines will be reported later.

The mercury lines 5790 to 3125A were compared with neon standards, the same tube being the source of both spectra, assuring simultaneity of exposure and identity of optical path. The strong mercury lines all appear to be complex; it is therefore of interest to see what accuracy can be expected in the measurement of these lines when the source is a low pressure tube. When weakly exposed these lines are usually single, or one component is notably stronger than the others. At some orders of interference the components of a line are grouped so as to show an unsymmetrical pattern which may be shaded to either shorter or longer values.[2] In such cases an effort was made to set on the center of gravity of the pattern, the apparent position of which shifts with the strength of exposure. The exact position of the apparent center depends not only on the strength of exposure, but also on the order of interference, on the reflectivity of the interferometer plates, on the grain of the photographic plate, and on the adjustment of the optical system. To evaluate the effect of each of these factors would require more observation than is warranted. The tables as published are the means of measurements of lines on exposures so short that the lines are barely visible, on normal exposures, and on exposures ten times as long as required for best results. All measurements were given equal weight regardless of strength of exposure, but the results from small separations were given half-weight if those from 25 and 40 mm were good.

TABLE III. Wave-lengths in the spectrum of mercury (Hg I) relative to neon standards.

| λ A in air | Vacuum wave No. Observed | Comp. | Level combinations | No. obs. | M.I.T. λ fraction A |
|---|---|---|---|---|---|
| 5790.6630 | 17264.405 | 0.401 | $6p\,^1P_1°-6d\,^1D_2$ | 14 | 0.654 |
| 5789.664*C* | 17267. | 0.383 | $6p\,^1P_1°-6d\,^3D_1$ | *C* | 0.66– |
| 5769.5982 | 17327.435 | 0.439 | $6p\,^1P_1°-6d\,^3D_2$ | 12 | 0.59– |
| 5460.7348 | 18307.479 | 0.479 | $6p\,^3P_2°-7s\,^3S_1$ | 23 | 0.740 |
| 4916.068– | 20335.799 | 0.809 | $6p\,^1P_1°-8s\,^1S_0$ | 2 | 0.036 |
| 4358.3277 | 22938.156 | 0.156 | $6p\,^3P_1°-7s\,^3S_1$ | 25 | 0.35– |
| 4347.4945 | 22995.312 | 0.316 | $6p\,^1P_1°-7d\,^1D_2$ | 19 | 0.496 |
| 4339.2232 | 23039.145 | 0.136 | $6p\,^1P_1°-7d\,^3D_2$ | 15 | 0.235 |
| 4108.054– | 24335.585 | 0.606 | $6p\,^1P_1°-9s\,^1S_0$ | 1 | 0.066 |
| 4077.8314 | 24515.943 | *S* | $6p\,^3P_1°-7s\,^1S_0$ | 14 | 0.811 |
| 4046.5630 | 24705.376 | 0.376 | $6p\,^3P_2°-7s\,^3S_1$ | 25 | 0.561 |
| 3906.371– | 25591.985 | 0.004 | $6p\,^1P_1°-8d\,^1D_2$ | 2 | 0.410 |
| 3901.868– | 25621.518 | 0.519 | $6p\,^1P_1°-8d\,^3D_2$ | 2 | 0.903 |
| 3801.6583 | 26296.872 | *S* | $6p\,^1P_1°-10s\,^1S_0$ | 2 | 0.658 |
| 3704.1655 | 26988.983 | 0.968 | $6p\,^1P_1°-9d\,^1D_2$ | 2 | 0.18– |
| 3663.2793 | 27290.202 | 0.205 | $6p\,^3P_2°-6d\,^1D_2$ | 29 | 0.276 |
| 3662.879*C* | 27293. | 0.187 | $6p\,^3P_2°-6d\,^3D_1$ | *C* | 0.878 |
| 3654.8363 | 27353.242 | 0.243 | $6p\,^3P_2°-6d\,^3D_2$ | 31 | 0.833 |
| 3650.1533 | 27388.334 | *D* | $6p\,^3P_2°-6d\,^3D_3$ | 43 | 0.146 |
| 3341.4766 | 29918.321 | 0.321 | $6p\,^3P_2°-8s\,^3S_1$ | 24 | 0.478 |
| 3131.8391 | 31920.900 | 0.882 | $6p\,^3P_2°-6d\,^1D_2$ | 5 | 0.833 |
| 3131.5485 | 31923.862 | 0.864 | $6p\,^3P_1°-6d\,^3D_1$ | 8 | 0.546 |
| 3125.6681 | 31983.920 | 0.920 | $6p\,^3P_1°-6d\,^3D_2$ | 12 | 0.663 |

The lines 4358, 3650, and 3341A were observed as traces in a neon tube during the first one or two hours of its use, and in a cadmium lamp. A few results from 3.75 or 5-mm separations of plates are compared with the adopted values in angstroms:

| | | | |
|---|---|---|---|
| Adopted | 4358.3277A | 3650.1533A | 3341.4766A |
| Trace | .3271(wt. 2) | .1536(wt. 2) | .4779(wt. 1). |

The agreement of "adopted" and "trace" is within the error to be expected of such low weights.

In the region compared directly with neon standards there are three well observed pairs of mercury lines

TABLE III-A. Additional lines in the spectrum of Hg I. Various standards.

| λ A in air | Vacuum wave No. Observed | Comp. | Level combinations | No. obs. | M.I.T. λ fraction A |
|---|---|---|---|---|---|
| 3027.487 | 33021.11 | 0.12 | $6p\,^3P_2°-7d\,^1D_2$ | 3 | 0.496 |
| 3025.606 | 33041.64 | 0.64 | $6p\,^3P_2°-7d\,^3D_1$ | 2 | 0.617 |
| 3023.475 | 33064.92 | 0.94 | $6p\,^3P_2°-7d\,^3D_2$ | 12 | 0.476 |
| 3021.498 | 33086.56 | *D* | $6p\,^3P_2°-7d\,^3D_3$ | 12 | 0.499 |
| 2967.543 | 33688. | 0.10 | $6p\,^3P_0°-6d\,^1D_2$ | *C* | 0.592 |
| 2967.280 | 33691.09 | 0.08 | $6p\,^3P_0°-6d\,^3D_1$ | 8 | 0.278 |
| 2925.410 | 34173.27 | 0.28 | $6p\,^3P_2°-9s\,^3S_1$ | 6 | 0.406 |
| 2893.594 | 34549.00 | 0.00 | $6p\,^3P_1°-8s\,^3S_1$ | 11 | 0.595 |
| 2856.935 | 34992.29 | 0.29 | $6p\,^3P_1°-8s\,^1S_0$ | 2 | 0.969 |
| 2806.759 | 35617.81 | 0.81 | $6p\,^3P_2°-8d\,^1D_2$ | 2 | 0.84– |
| 2805.344 | 35635.77 | 0.73 | $6p\,^3P_2°-8d\,^3D_1$ | 2 | 0.42– |
| 2804.434 | 35647.34 | 0.33 | $6p\,^3P_2°-8d\,^3D_2$ | 2 | 0.462 |
| 2803.465 | 35659.66 | *D* | $6p\,^3P_2°-8d\,^3D_3$ | 12 | 0.472 |
| 2759.706 | 36225.08 | 0.09 | $6p\,^3P_2°-10s\,^3S_1$ | 2 | 0.712 |
| 2752.778 | 36316.22 | 0.22 | $6p\,^3P_0°-8s\,^3S_1$ | 2 | 0.775 |
| 2699.514 | 37032.74 | *D* | $6p\,^3P_2°-9d\,^3D_2$ | 2 | 0.50– |
| 2698.828 | 37042.15 | *D* | $6p\,^3P_2°-9d\,^3D_3$ | 5 | 0.851 |
| 2674.908 | 37373.38 | *S* | $6p\,^3P_2°-11s\,^3S_1$ | 1 | 0.99– |
| 2655.127 | 37651.81 | 0.81 | $6p\,^3P_1°-7d\,^1D_2$ | 10 | 0.121 |
| 2653.679 | 37672.33 | 0.33 | $6p\,^3P_1°-7d\,^3D_1$ | 10 | 0.681 |
| 2652.039 | 37695.63 | 0.63 | $6p\,^3P_1°-7d\,^3D_2$ | 11 | 0.042 |
| 2641.1— | 37852.— | | $6p\,^3P_2°-10d\,^3D_1$ | — | 0.11– |
| 2639.780 | 37870.68 | *D* | $6p\,^3P_2°-10d\,^3D_2$ | 2 | 0.93*w* |
| 2625.192 | 38081.10 | *S* | $6p\,^3P_2°-12s\,^3S_1$ | 2 | 0.24– |
| 2603.— | 38403.— | | $6p\,^3P_2°-11d\,^3D_2$ | — | 0.15*w* |
| 2578.912 | 38764.44 | *D* | $6p\,^3P_2°-12d\,^1D_2$ | 1 | 0.91– |
| 2576.285 | 38803.97 | 0.96 | $6p\,^3P_1°-9s\,^3S_1$ | 6 | 0.295 |
| 2563.855 | 38992.09 | 0.09 | $6p\,^3P_1°-9s\,^1S_0$ | 2 | 0.90– |
| 2536.517 | 39412.30 | *S* | $6p\,^3P_1°-6s^2\,^1S_0$ | 2 | 0.519 |
| 2534.764 | 39439.55 | 0.55 | $6p\,^3P_0°-7d\,^3D_1$ | 10 | 0.775 |
| 2483.815 | 40248.50 | 0.48 | $6p\,^3P_1°-8d\,^1D_2$ | 2 | 0.829 |
| 2482.710 | 40266.41 | 0.41 | $6p\,^3P_1°-8d\,^3D_1$ | 3 | 0.721 |
| 2481.996 | 40277.99 | 0.00 | $6p\,^3P_1°-8d\,^3D_2$ | 5 | 0.008 |
| 2464.057 | 40571.20 | 0.18 | $6p\,^3P_0°-9s\,^3S_1$ | 2 | 0 068 |
| 2446.895 | 40855.76 | 0.76 | $6p\,^3P_1°-10s\,^3S_1$ | 2 | 0.905 |
| 2441.062 | 40953. | 0.35 | $6p\,^3P_1°-10s\,^1S_0$ | *C* | 0.03– |
| 2400.493 | 41645.42 | 0.45 | $6p\,^3P_1°-9d\,^1D_2$ | 1 | 0.52– |
| 2399.727 | 41658.71 | 0.73 | $6p\,^3P_1°-9d\,^3D_1$ | 1 | 0.74– |
| 2399.453 | 41663. | 0.41 | $6p\,^3P_1°-9d\,^3D_2$ | *C* | 0.379 |
| 2379.996 | 42004. | 0.05 | $6p\,^3P_1°-11s\,^3S_1$ | *C* | 0.990 |
| 2378.316 | 42033.72 | 0.63 | $6p\,^3P_0°-8d\,^3D_1$ | 1 | 0.33– |
| 2352.— | 42495. | — | $6p\,^3P_1°-10d\,^3D_2$ | — | 0.48*h* |
| 2345.433 | 42622. | 0.98 | $6p\,^3P_0°-10s\,^3S_1$ | *C* | 0.431 |
| 2340.566 | 42711. | 0.78 | $6p\,^3P_1°-12s\,^3S_1$ | *C* | 0.55– |
| 2323.197 | 43030.90 | *D* | $6p\,^3P_1°-11d\,^3D_2$ | 1 | 0.20– |
| 2302.059 | 43425.98 | 0.95 | $6p\,^3P_0°-9d\,^3D_1$ | 1 | 0.09*h* |
| 2247.553 | 44479. | 0.00 | $6p\,^3P_0°-12s\,^3S_1$ | *C* | 0.70– |

whose wave numbers differ by the interval $6p\,^3P_2^\circ$–$6p\,^3P_2^\circ$; in view of the experience of previous observers we were surprised and gratified to find the agreement shown here.

| λ A | Wave No. | λ A | Wave No. | λ A | Wave No. |
|---|---|---|---|---|---|
| 5460 | 18307.479 | 3654 | 27353.242 | 3341 | 29918.321 |
| 4358 | 22938.156 | 3125 | 31983.920 | 2893 | 34548.997 |
| Diff. ($cm^{-1}$) | | 4630.677 | 4630.678 | | 4630.676 |

The close agreement is of course accidental.

Some of the short wave neon lines have been observed by means of nine different separations, 3.75 to 40 mm. The median variation of wave-length with thickness is about a part in seven million, the extreme range being a part per two million. There is no systematic variation as great as the accidental error. With the exception of those involving an *s* level the well observed mercury lines are nearly as good in this respect as those of neon. These exceptional (and strongest) lines in the spectrum of natural mercury vary more widely than the others with change of interferometer; the $6p\,^3P_{2,1,0}^\circ$–$7s\,^3S_1$ and $6p\,^3P_1^\circ$–$7s\,^1S_0$ of natural mercury are not suitable for standards when an accuracy exceeding a part per million is required.

Kayser's *Handbuch*[8] records the comparisons of mercury lines with the fundamental standard which were made before 1927. More recently, Pérard[9] has compared certain mercury lines with the cadmium standard with higher accuracy than was attained earlier. Pérard varied the resolution from moderate to high and considered the published wave-lengths to refer to the strongest component of each line. We have determined accurate wave-lengths for four of these lines; ours are probably center of gravity values. Pérard and Terrien[10] report the preliminary results of the observation of three of these lines with $Hg^{198}$ as source. The means of the measurements made by Meggers, by Barrell, and by Pérard and Terrien are shown in the fourth column below.

| | Natural mercury | | $Hg^{198}$ | Level |
|---|---|---|---|---|
| λ A | Pérard | *AOW* | mean | combinations |
| 5790 | 0.6638A | 0.6630A | 0.6629A | $6p\,^1P_1^\circ$–$6d\,^1D_2$ |
| 5769 | 0.5996 | 0.5982 | 0.5985 | $6p\,^1P_1^\circ$–$6d\,^3D_2$ |
| 5460 | 0.7430 | 0.7348 | 0.7532 | $6p\,^3P_2^\circ$–$7s\,^3S_1$ |
| 4358 | 0.3250 | 0.3277 | | $6p\,^3P_1^\circ$–$7s\,^3S_1$ |

The close agreement of observations made under different conditions of excitation and with different isotopes as sources suggests that the $6p\,^1P_1^\circ$–$6d\,^1D_2$ and $6p\,^1P_1^\circ$–$6d\,^3D_2$ may be used as standards; the wave-lengths of $6p\,^3P_{2,1}^\circ$–$7s\,^3S_1$ vary so much with observing conditions that no precise value can be assigned to them when natural mercury is the source.

The region shorter than 3100A was observed by means of one pair of interferometer plates, crystal quartz thinly coated with aluminum. Etalons of length 2, 3.75, 5, and 8 mm were used. The thickness was determined by use of lines recently measured and two lines given by Meggers and Burns,[11] *viz.*, 3080.827 and 2980.622A of cadmium. The new lines are 3261.054, 3252.524, and 3133.167 of cadmium; 3125.668 of mercury; 3148.610, 3153.411, and 3167.575 of neon. The agreement between standards was not entirely satisfactory and agreement from plate to plate was also rather poor. The phase change 3200 to 2300A is large and poorly determined. But it does not seem wise to expend any more effort on this region of the spectrum of natural mercury since 2536A is probably the only line that will show as a trace in low pressure observations of other elements and this line is rather too complex for precise measurement with natural mercury as source. Because of uncertainty in the phase change, wave-lengths in the region shorter than 2893A were adjusted to agree with levels derived from longer wave-lengths. In this region our adjusted values are probably more accurate than our observed.

In Table III the column headed "M.I.T." contains wave-lengths as published by Harrison[12] and others in 1939. The editors of this table selected the best available values; some were measured at M.I.T. Some of these wave-lengths apply to the arc in air, some to the arc at reduced pressure, and some to low pressure (vacuum). In general, the M.I.T. table lends support to our wave-lengths where we have no check. In four or five cases the reality of our line and the level depending on it may be questioned.

We are indebted to the National Bureau of Standards for the loan of interferometer plates, neon tubes, and separators; and to E. U. Condon, W. F. Meggers, and Charlotte Moore Sitterly for encouragement and assistance. We thank R. F. Mehl and the Carnegie Institute of Technology for the loan of the quartz spectrograph which was necessary for much of our work.

TABLE IV. The lower levels of Hg I.

| | | | |
|---|---|---|---|
| | Even | | |
| $6s^2\,^1S_0$ 0.000 | | | $6d\,^1D_2$ 71333.182 |
| $7s\,^1S_0$ 63928.243* | $7s\,^3S_1$ 62350.456 | | $7d\,^1D_2$ 77064.097 |
| $8s\,^1S_0$ 74404.590 | $8s\,^3S_1$ 73961.298 | | $8d\,^1D_2$ 79660.785 |
| $9s\,^1S_0$ 78404.387 | $9s\,^3S_1$ 78216.261 | | $9d\,^1D_2$ 81057.749 |
| $10s\,^1S_0$ 80365.653* | $10s\,^3S_1$ 80268.056 | | $10d\,^1D_2$ ..... |
| | $11s\,^3S_1$ 81416.352* | | $11d\,^1D_2$ ..... |
| | $12s\,^3S_1$ 82124.081* | | $12d\,^1D_2$ 82807.421* |
| $6d\,^3D_1$ 71336.164 | $6d\,^3D_2$ 71396.220 | | $6d\,^3D_3$ 71431.311* |
| $7d\,^3D_1$ 77084.632 | $7d\,^3D_2$ 77107.917 | | $7d\,^3D_3$ 77129.535* |
| $8d\,^3D_1$ 79678.708 | $8d\,^3D_2$ 79690.300 | | $8d\,^3D_3$ 79702.634* |
| $9d\,^3D_1$ 81071.027 | $9d\,^3D_2$ 81075.713* | | $9d\,^3D_3$ 81085.126* |
| | | | $10d\,^3D_3$ 81913.632* |
| | Odd | | |
| $6p\,^3P_0^\circ$ 37645.080 | $6p\,^3P_1^\circ$ 39412.300 | $6p\,^3P_2^\circ$ 44042.977 | $6p\,^1P_1^\circ$ 54068.781 |

* No check.

*Note.*—The odd levels and the even levels $7s\,^1S_0$, $7s\,^3S_1$, $8s\,^1S_0$, $6d\,^1D_2$, $6d\,^3D_2$ and $6d\,^3D_3$ were evaluated from lines which have been directly compared with neon twelve or more times. These levels are probably sufficiently accurate to warrant the use of eight places. The relative values of some other levels appear to be sufficiently consistent to justify the use of eight places. The level designations follow those of R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

[8] H. Kayser, *Handbuch der Spectroscopie* **7**, 669 (1934).
[9] A. Pérard, Rev. d'Optique **7**, 1 (1928).
[10] A. Pérard and J. Terrien, Comptes Rendus **228**, 964 (1949).
[11] W. F. Meggers and K. Burns, Sci. Papers Bur. Stand. **18**, 185 (1922), SP 441.
[12] G. R. Harrison, *MIT Wavelength Tables* (John Wiley and Sons, Inc., New York, 1939).

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# Interferometric Measurements of Wave-Lengths in the Spectrum of Mercury Isotope 198*

JOHN M. BLANK
*Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts*
(Received February 23, 1950)

Six lines in the spectrum of $Hg^{198}$ in the range 5790 to 3650A have been measured with Fabry-Perot etalons. The wave-lengths obtained were 5790.6627, 5769.5984, 5460.7531, 4358.3376, 4046.5716, and 3650.1569A. These results are compared with those previously reported.

IN 1940 it was reported by Wiens and Alvarez[1] that $Hg^{198}$ could be excited to emit radiation free from isotopic and hyperfine structure. Meggers[2] in 1948 recommended the use of the 5461A line of $Hg^{198}$ as a possible standard of length.

Preliminary measurements of the wave-lengths of the two yellow lines and of the green line of $Hg^{198}$ by Pérard and Terrien in France, by Barrell in England, and by Meggers at the National Bureau of Standards have been reported by Pérard and Terrien.[3] Further measurements are here offered as a check on the reproducibility of the green line.

The $Hg^{198}$ lamp, kindly furnished by the National Bureau of Standards, was similar to those used by the other investigators and described by Pérard and Terrien.[3] The lamp used in the present work was excited by a 150-Mc/sec. oscillator and was water-cooled to about 25°C. A cadmium lamp of the Michelson type was used for comparison and was operated under standard conditions.[4]

The dispersion of the Fabry-Perot interferometer was crossed with that of a 35-ft. grating in a Wadsworth stigmatic mounting. The Fabry-Perot interferometer was illuminated by the external parallel beam method with auxiliary slit, as described by Tolansky.[5] This method completely eliminates secondary or "ghost" patterns. An image of the $Hg^{198}$ lamp was projected inside the cadmium lamp at unit magnification. The combined image of both sources was then projected on the auxiliary slit.

The quartz etalon mirrors were coated with silver to a thickness which permitted transmission of only five percent of the incident light. This gave high resolving power and produced exceedingly sharp fringes which could be measured with high accuracy. The construction of the etalon spacers and etalon holder, the etalon chamber, and the constant temperature bath have been described by Newbound.[6]

The etalon chamber was evacuated and flushed with dry air before any final photographs were made. Air was admitted through a tube of silica gel and the etalon chamber was allowed to come to atmospheric pressure, then closed off with a stopcock before the start of each exposure. The pressure inside the etalon chamber was then taken to be the same as that read from a barometer in the room. Appropriate temperature corrections[7] were applied to the barometer readings.

Photographs were obtained in two regions, both chosen to include the cadmium red line. The first region extended from 4500 to 7000A and thus contained 5461, 5770, 5791, and 6438A. The second region extended from 6400 to 9000A and thus contained 6438, and in the second order, 3650, 4047, and 4358A.

The spacers used for these measurements were 4.3, 7.5, and 25 mm thick. At least four spectrograms were obtained in each of the two regions for each spacer. The diameters of six rings in the interference pattern of each line were measured four times on a Hilger comparator, and the average was used in the calculations.

The wave-length calculations followed a method described by Meissner,[8] based on one by St. John, which does not require a knowledge of the magnification of the spectrograph nor of the focal length of the projection lens. Six rings were used to calculate the fractional order of interference at the center of each pattern and from this the etalon separation and the wave-lengths were calculated for each plate.

Since the air pressure in the etalon chamber was reduced to atmospheric at the beginning of each exposure, it was in general different for each exposure. Accordingly the wave-lengths were corrected for the dispersion of the index of refraction of air to reduce them to their values in standard air (15°C and 760 mm of mercury). The corrections used were obtained from the tables of Meggers and Peters.[9] No correction was applied for the presence of carbon dioxide in excess of the amount present in standard air, since the air-conditioned laboratory was believed to not contain an excess of carbon dioxide.

The wave-lengths reduced to standard air were used

* Based on a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science.

[1] J. H. Wiens and L. W. Alvarez, Phys. Rev. **58**, 1005 (1940).
[2] W. F. Meggers, J. Opt. Soc. Am. **38**, 7 (1948).
[3] A. Pérard and J. Terrien, Comptes Rendus **228**, 964 (1949).
[4] Trans. Int. Union Solar Res. **2**, 109 (1907).
[5] S. Tolansky, *High Resolution Spectroscopy* (Methuen and Company, Ltd., London, 1947), p. 153.
[6] K. B. Newbound, J. Opt. Soc. Am. **39**, 835 (1949).
[7] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1941), p. 1804.
[8] W. K. Meissner, J. Opt. Soc. Am. **31**, 405 (1941).
[9] W. F. Meggers and C. G. Peters, Bull. Bur. Stand. **14**, 728 (1919).

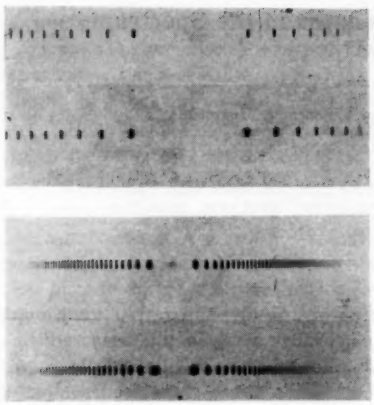


FIG. 1. Interference fringes of the green line of $Hg^{198}$ at 5461A and the red line of Cd at 6438A with etalon separations of 4.3 mm (A) and 25 mm (B).

to obtain an average value for each wave-length at each of the three etalon separations. These three values were then used in pairs, the 4.3-mm values with the 25-mm values and the 7.5-mm values with the 25-mm values, to correct for the dispersion of phase change at reflection. A correction term was then added to each wave-length. Meissner[8] has discussed this correction in the form

$$\Delta\lambda''=\frac{(\lambda''-\lambda')t_1}{t_2-t_1},\quad \Delta\lambda'=\frac{(\lambda''-\lambda')t_2}{t_2-t_1},$$

where $\lambda''$ is the wave-length obtained for the etalon spacer $t_2$, $\lambda'$ is the wave-length obtained for the etalon spacer $t_1$, and $\Delta\lambda''$ and $\Delta\lambda'$ are the corrections to be added to $\lambda''$ and $\lambda'$, respectively.

It is important to notice that much accuracy can be lost unless a proper set of etalon separations is chosen. Although only small corrections are added to wave-lengths obtained for large etalon separation, the temptation to choose only large separations must be avoided. As a graphic example, let us suppose that two large separations of exactly 50.00 and 60.00 mm have been used and the wave-lengths at these separations determined with a standard deviation of ±0.0002A. One might expect the values

4046.5712A at 50.00 mm
4046.5713A at 60.00 mm.

The standard deviation of the difference (4046.5713 −4046.5712) is

$$[(0.0002)^2+(0.0002)^2]^{\frac{1}{2}}=0.0003.$$

Assuming that the separations are known exactly, we have

$$\Delta\lambda''=(0.0001\pm0.0003)50/(60-50)$$
$$=0.0005\pm0.0015$$

which is so uncertain as to be worthless. But suppose, on the other hand, we use separations of 5.00 and 50.00 mm, for which we might expect

4046.5649A at 5.00 mm
4046.5712A at 50.00 mm.

Then

$$\Delta\lambda''=(0.0063\pm0.0003)5/(50-5)$$
$$=0.0007\pm0.00003$$

and

$$\Delta\lambda'=(0.0063\pm0.0003)50/(50-5)$$
$$=0.0070\pm0.0003,$$

which is satisfactory. Thus it is not desirable to use large separations alone.

As is seen in Fig. 1, six sharp rings were available at 4.3-mm separation and could be measured with as much precision as those at 25 mm.

In Table I the results of this investigation are compared to the results previously published by other workers.

TABLE I.

| Meggers[a] | Barrell[a] | Pérard and Terrien[a] | Present paper |
|---|---|---|---|
| 5790.6628 | 5790.6628 | 5790.6630 | 5790.66272±0.00008[b] |
| 5769.5983 | 5769.5985 | 5769.5986 | 5769.59836±0.00013 |
| 5460.7532 | 5460.7531 | 5460.7533 | 5460.75313±0.00009 |
| | | | 4358.33763±0.00009 |
| | | | 4046.57161±0.00006 |
| | | | 3650.15688±0.00012 |

[a] See reference 3.
[b] Standard deviations.

The wave-lengths in the first three columns were given as preliminary values only. In the work of Pérard and Terrien the wave-lengths were measured relative to the cadmium red line using a Michelson interferometer rather than a Fabry-Perot interferometer.

The author wishes to express his thanks to G. R. Harrison for suggesting this problem and for his encouragement and supervision of the experimental work, and to W. F. Meggers of the National Bureau of Standards for furnishing the $Hg^{198}$ lamp and for making suggestions on the choice of an exciter unit.

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# Dependence of Emission Spectra of Phosphors upon Activator Concentration and Temperature

GORTON R. FONDA
*Research Laboratory, General Electric Company, Schenectady, New York*
(Received February 13, 1950)

Two groups of oxygen-containing phosphors are examined for the effect of activator concentration and temperature upon the location of their peak emission. The first group includes five phosphors whose emission is distributed between two main spectral bands to an extent dependent on activator concentration. Sufficient decrease in activator content causes all of the emission to appear in the shorter wave-length band. An increase in temperature has the same effect. In the second group, represented by three phosphors, the emission cannot be resolved into component bands by change in activator content. An increase in temperature shifts the emission to shorter wave-length.

A CHANGE in the temperature of a phosphor has been observed to lead to a change in the spectral distribution of its emission. Before concluding that this denotes a change in location of a single, unique emission band, it seems well to consider if the emission process may not involve multiple bands more frequently than has been suspected and that the effect of temperature is to alter the proportion of excited energy which is radiated in the component bands. Such a case is illustrated by the zinc beryllium silicate phosphor.[1] This query has been previously raised.[2] In order to obtain additional evidence bearing upon it, further and more extensive measurements have been made on the spectral distribution of oxygen-containing phosphors as affected by activator concentration and temperature.

The fact that multiple emission may occur even with a single activator is now established. In recent years observations have been accumulating that the emission spectrum of a phosphor may undergo extensive changes as the result of alterations in activator concentration.[1,3–6] Examples are furnished by the alkaline halides activated with thallium, calcium oxide activated with lead, and calcium silicate, zinc silicate, zinc beryllium silicate and magnesium silicate activated with manganese. These phosphors are characterized by an emission in which two separate bands are clearly evident. In all of them, a high activator concentration causes the long wave-length band to predominate. When the activator concentration is lowered, the intensity of the long wave-length band is reduced and the short wave-length band develops and becomes so intensified that ultimately the longer wave-length band virtually disappears. Such results demonstrate that the excited energy is capable of emission in two separate bands and that its distribution between these bands depends upon the concentration of the activator.

In the case of two of these phosphors, calcium silicate and zinc beryllium silicate, it has been shown that an increase in temperature has a similar effect on the emission as a decrease in activator concentration, namely, to reduce and ultimately to suppress the long wave-length band and to intensify the short wave-length band.[1,7] Studer and Gaus observed also that the emission band of magnesium tungstate was shifted to shorter wave-lengths as its temperature was increased.

Such temperature dependence raises the suspicion that the emission of a phosphor, which is reputed to lie in a single band, may actually comprise two component bands, so close together that, at any one temperature, they merge into what appears to be a single band. If duplex emission of this type is in fact involved, such a phosphor should show a shift to shorter wave-

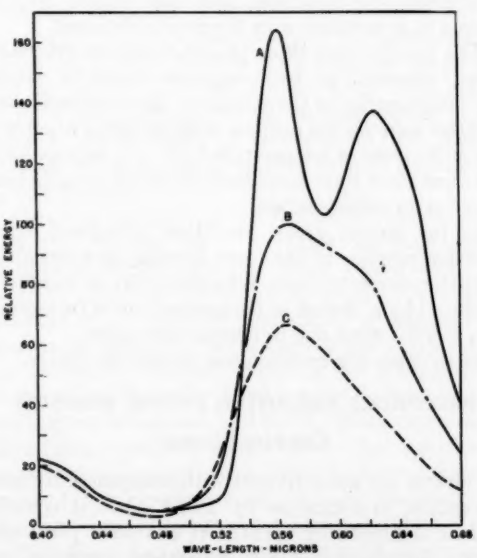


FIG. 1. Emission spectra of calcium silicate activated with lead and 0.2 percent Mn and its dependence upon temperature. A—80°K, B—300°K, C—475°K.

[1] F. J. Studer and L. Gaus, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948), p. 258.
[2] G. R. Fonda, J. Electrochem. Soc. **96**, 43C (1949).
[3] W. von Meyeren, Zeits. f. Physik **61**, 321 (1930).
[4] W. Bünger and W. Flechsig, Zeits. f. Physik **69**, 637 (1932).
[5] G. R. Fonda and H. C. Froelich, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948), p. 385.
[6] S. H. Patten and F. E. Williams, J. Opt. Soc. Am. **39**, 702 (1949).
[7] F. J. Studer and G. R. Fonda, J. Opt. Soc. Am. **39**, 656 (1949).

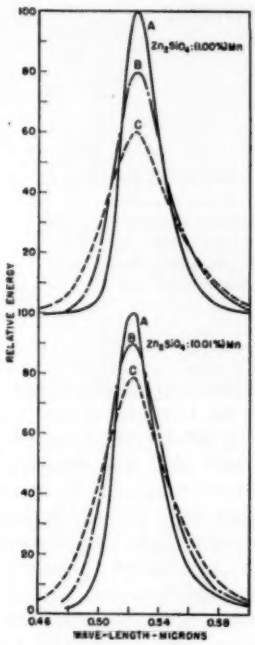


FIG. 2. Dependence of emission spectra upon temperature for zinc orthosilicate activated with manganese. A—80°K, B—300°K, C—470°K.

length in the location of its emission band when the concentration of the activator is reduced as well as when the temperature is raised.

The present experiments were undertaken on well-known phosphors to find what basis there is for such a possibility. The phosphors have been divided into two groups in accordance with the results obtained.

The first includes those phosphors whose emission is clearly resolved into two component bands by varying the concentration of the activator. Measurements made on them were for the purpose of establishing whether or not an increase in temperature leads to a segregation of the same short wave band that is isolated by a decrease in activator concentration.

In the second group are those phosphors whose emission persists in the same spectral location at all activator concentrations. Whatever shift in location is produced by a change in temperature must be ascribed to a specific effect due to temperature alone.

In all cases, the emission was excited by 2537A.

## PHOSPHORS EXHIBITING DUPLEX EMISSION

### Calcium Silicate

Calcium silicate activated with manganese becomes susceptible to excitation by 2537A when it contains lead as a sensitizing agent.[6] As has been previously shown, the emission due to manganese comprises two bands, at 5600 and 6200A. The 5600A band is intensified and the 6200A partially suppressed by reduction in the concentration of manganese.[6,7] It has been shown also that increase in temperature had the apparent effect of shifting the emission to shorter wave-lengths. At concentrations of both 1.6 percent Mn and 5.0 percent Mn, the temperature rise seemed to isolate a single band at 5600A, the location of the short wave band characteristic of low manganese at room temperature. It remains to show that this location is stable and represents the minimum attainable.

Phosphors were made with particularly low manganese content. At 0.20 percent Mn accurate records of spectral distribution could be obtained up to 475°K. The results are shown in Fig. 1. The high resolution obtainable in liquid air gave a location of 5600A for the shorter wave-length band and 6240A for the longer, both in agreement with the measurements previously reported. As the temperature was raised to 475°K, the longer wave-length band was increasingly lowered in intensity. The position of the shorter band remained set, close to 5600A. Measurements of phosphors containing 0.10 and 0.05 percent Mn were made up to 370°K and gave identical results.

It can therefore be concluded that 5600A is not only the minimum peak location of emission that can be obtained by reduction in activator concentration but that it coincides with the stable location of the minimum wave-length band that may be obtained by increase in temperature.

### Zinc Beryllium Silicate

After the extensive work of Studer and Gaus on the effects produced by changes in composition and temperature,[1] hardly anything more remains to be done. For the sake of the argument, however, note should be made that these investigators found that the emission due to manganese is comprised in two bands, a long wave-length band whose peak is in the neighborhood of 6100A and a short wave-length band whose peak is close to that of the green band in zinc orthosilicate at 5250A. Decrease in either manganese or beryllium depressed the 6100A band and intensified the 5250A band. Increase in temperature had the same effect.

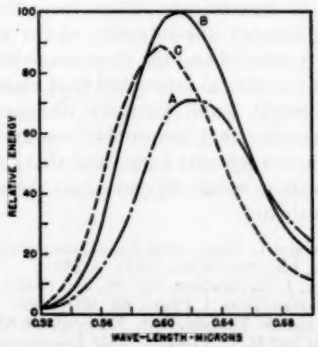


FIG. 3. Emission spectra at 25°C of cadmium silicate activated with various amounts of manganese. A—2.00 percent Mn, B—1.00 percent Mn, C—0.25 percent Mn.

[6] H. C. Froelich, J. Electrochem. Soc. 93, 101 (1948).

Again one concludes that 5250A is the ultimate location attainable for the shorter band by decrease in activator concentration or by increase in temperature.

### Zinc Orthosilicate

For practical purposes this phosphor, activated with manganese, is regarded as having a single band emission lying in the green at 5250A. Actually the phosphor exhibits double band emission. As discovered by Kroeger,[9] a red band appears with high manganese concentration in measurements at liquid air temperature. He points out that its position coincides with that of the long wave-length band in zinc beryllium silicate and that the function of beryllium is to render appreciable at room temperature what would otherwise be observable only at liquid air temperature. His observations have been confirmed by Nagy.[10]

It has been the contention of Szigeti, Nagy, and Makai[11] and of Butler[12] that the emission of the zinc silicate and the zinc beryllium silicate phosphors can be resolved into further subsidiary bands. For our purpose, attention can properly be confined to the two main bands. Under changes in temperature and in activator concentration, the subsidiary bands appear to follow the behavior of the main bands, in which they are elements.

If one regards then the green band of zinc silicate low in manganese as being the shorter wave component of a double band emission, it is important for our argument to establish that its position is stable and may not be shifted to still shorter wave-length by further reduction in manganese content or by increase in temperature. A series of phosphors was prepared with manganese contents of 1.00, 0.50, 0.30, 0.10, and 0.01 percent. At each one of these concentrations, the peak location of the emission band was found to lie at 5230–5250A for temperatures of 80°, 300°, 375°, and 470°K. Results for the extremes in composition are shown in the curves of Fig. 2.

The conclusion from these results is that the shorter of the two main bands retains its location at 5230–5250A at all temperatures and concentrations of manganese. Nagy came to the same conclusion.[10]

Two investigators have observed a shift in the location of this peak to slightly shorter wave-length on reducing the temperature from room temperature to that of liquid air. Shrader found it to change from 5275 to 5225A for a phosphor containing 0.3 percent manganese[13] and Vlam records a change from 5219 to 5206A for a sample containing 0.1 percent manganese.[14] We did not observe any change.

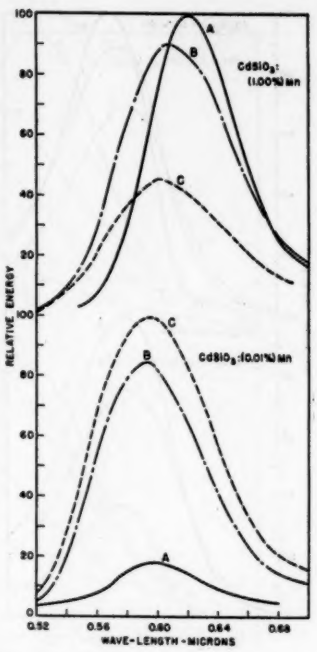


FIG. 4. Dependence of emission spectra upon temperature for cadmium silicate activated with manganese. A—80°K, B—300°K, C—390°K.

### Cadmium Silicate

Samples of this phosphor activated with manganese were prepared at 1100°C with 0.5 percent lithium chloride as a flux to facilitate the reaction. Tests were made with six different concentrations of manganese as activator, 2.00, 1.00, 0.50, 0.25, 0.10, and 0.01 percent by weight. Although this phosphor has been regarded as having a single emission band only, yet the peak of this band at 25°C was found to be shifted continuously by reduction in manganese content from 6240A at 2.00 percent Mn to 5950A at 0.10 percent Mn. Further decrease of the activator to 0.01 percent produced no further change.

Curves of the spectral distribution at room temperature are given in Fig. 3 for three concentrations of manganese which cover the range within which significant changes in spectral emission occur. Not only is the peak of the emission band shifted to shorter wavelengths by reduction in manganese concentration but the band width changes. At two percent manganese the width at half-intensity is 50 percent broader than at one percent manganese and below. These two observations taken together furnish evidence that the emission at two percent manganese is made up of two component bands, rather closely overlapping, and that their positions at room temperature are 6240 and 6000A.

The effect of changing temperature is shown in the curves of Fig. 4 for two contrasting concentrations of manganese. At one percent manganese the concentration is so high that both constituent bands are present at low temperatures; the shorter wave component with

[9] F. A. Kroeger, Physica **6**, 767 (1939).
[10] E. Nagy, J. Opt. Soc. Am. **39**, 42 (1949).
[11] G. Szigeti, E. Nagy, and E. Makai, J. Chem. Phys. **15**, 881 (1947).
[12] K. H. Butler, J. Electrochem. Soc. **93**, 143 (1948).
[13] R. E. Shrader, J. Opt. Soc. Am. **39**, 699 (1949).
[14] C. C. Vlam, Physica **15**, 609 (1949).

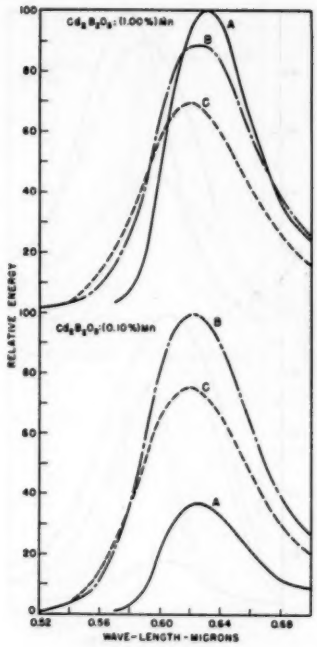


FIG. 5. Dependence of emission spectra upon temperature for cadmium borate activated with manganese. A—80°K, B—300°K, C—375°K.

a peak at 6000A is isolated at high temperature. At the low concentration of 0.01 percent manganese, the position of this shorter wave component is more accurately shown to be 5950A. Its position is not altered by an increase in temperature.

In conformity with the behavior of the phosphors described above, therefore, an increase in temperature serves to isolate the same shorter wave component at high manganese concentration which is characteristic of the emission for low manganese content at all temperatures.

### Cadmium Borate

This phosphor has also been regarded as having only a single emission band. It was prepared from a mixture of two moles of cadmium oxide and two moles of boric acid with various amounts of manganese, introduced as carbonate. It was fired at 875°C. The manganese content ranged from 1.00 to 0.02 percent Mn by weight. Curves of its spectral distribution give evidence of two constituent emission bands, as with cadmium silicate. The two bands however are considerably closer together. Above 0.50 percent Mn, the peak of the emission at 80°K lies at 6300A and is reduced to 6200A on sufficient increase in temperature. Below 0.10 percent Mn, the peak is altered only insignificantly by change in temperature and persists at the stable value of 6200A. 6200A is therefore to be accepted as the position of the shorter wave-length band and 6300A, that of the longer wave-length band.

The effects of temperature are shown in the curves of Fig. 5 for two contrasting concentrations of manganese. Again, the results are in accord with the previous cases discussed.

## PHOSPHORS WITH SINGLE BAND EMISSION

### Zinc Fluoride

This phosphor is activated with manganese. Its emission under excitation by 2537A is sensitized by titanium. Titanium is also an activator and the peak of its emission band at room temperature is close to that of the manganese band.[15] Its emission is much weaker than that of manganese and is suppressed in the presence of normal concentrations of manganese.

Emission curves are given in Fig. 6 for two phosphors sensitized by titanium. The emission curves for 1.0 percent Mn are characteristic of manganese emission alone. At the low content of 0.1 percent Mn, the emission bands are considerably broader. This is due to the presence also of some titanium emission, whose band is extremely broad.

At any one temperature, the peak location is virtually identical for both the high and the low concentration of manganese. This is in contrast to the behavior of phosphors described in the previous section. When, however, the temperature is reduced, the peak emission is shifted to shorter wave-lengths. In this case therefore temperature alone has a specific effect in altering the location of an emission band.

### Calcium Fluorphosphates

These phosphors are the recent discovery of McKeag and Ranby.[16] When activated by antimony alone, their emission lies in the blue. When manganese is present as well, its characteristic emission is sensitized by the antimony and a separate manganese emission band appears in the red. The blue antimony band is suppressed to an extent dependent on the manganese concentration.

The calcium halophosphate phosphors have the constitution of the mineral apatite and may contain either the chloride or fluoride of calcium. Their characteristics are similar. The only significant difference is that the emission of the chlorphosphate lies further to the red. For the purpose of these measurements the fluorphosphate was chosen. It was prepared from mixtures of precipitated calcium acid phosphate, calcium carbonate and calcium fluoride in such proportions as to yield, after firing at 1170°C, the compound $3Ca_3(PO_4)_2 \cdot CaF_2$. The activators were added as antimony oxide and manganese ammonium phosphate. The firing was carried out in a quartz tube closed at the end within the furnace and with a plug of glass wool in the open end which projected from the furnace. Considerable antimony is lost by vaporization during the firing operation.

[15] G. R. Fonda and F. J. Studer, J. Opt. Soc. Am. **38**, 1007 (1948).

[16] H. G. Jenkins, A. H. McKeag, and P. W. Ranby, J. Electrochem. Soc. **96**, 1 (1949).

The concentrations of activators cited in the text refer to the amounts introduced with reference to the amount of calcium fluorphosphate that would be formed in the reaction if no ingredients were lost.

The emission with antimony alone is shown in the curves of Fig. 7 for two extremes in concentration, 3.7 percent and 0.05 percent Sb. At any one temperature the location of the band peaks is closely the same at both concentrations. What is outstanding is the effect of temperature. An increase in temperature leads to an extreme shift in the peak location, much the greatest that has been observed with any phosphor. The extent of the shift is independent of the concentration of antimony.

The effect of variation in the manganese content is shown in the curves of Fig. 8. With the larger amount of manganese, 2.0 percent Mn, the antimony emission band is so much suppressed that it is without effect upon the shape of the manganese emission bands. With 0.5 percent Mn, on the other hand, the emission of the antimony predominates. This necessitates a correction to the manganese emission bands to allow for the contributions which they receive from the overlapping antimony bands, extending well out into the red, as shown in Fig. 7. When this correction is made, it is found that the peak location of the manganese band is not altered appreciably by change in manganese concentration but is shifted slightly to shorter wave-length by increase in temperature.

The extent of these effects is shown in Table I for these phosphors and others having intermediate concentrations.

The results from this phosphor agree therefore with those from the previous two phosphors. The locations of both the antimony and the manganese emission bands are not altered by change in activator concentration but are shifted to shorter wave-length on increase in temperature.

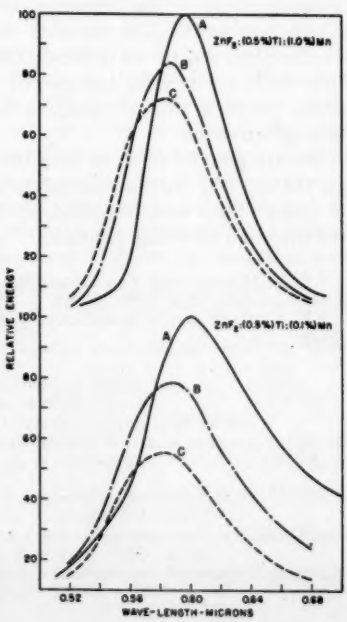


FIG. 6. Dependence of emission spectra upon temperature for zinc fluoride activated with titanium and manganese. A—80°K, B—300°K, C—375°K.

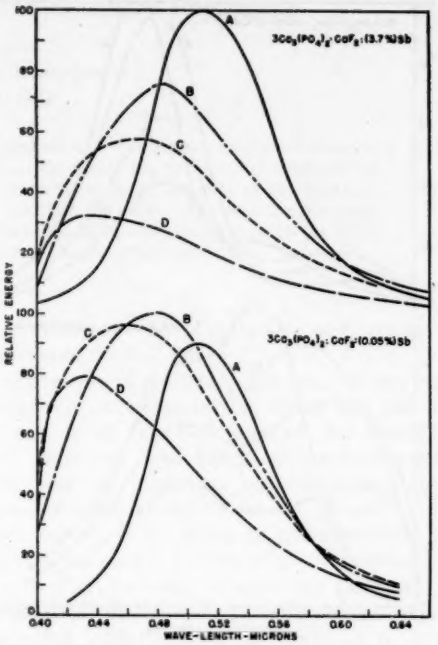


FIG. 7. Dependence of emission spectra upon temperature for calcium fluorphosphate activated with antimony. A—80°K, B—300°K, C—380°K, D—475°K.

## DISCUSSION

The purpose of this investigation was to find what coordination there might be between the effects of activator concentration and temperature upon the spectral emission of phosphors. The phosphors have been divided into two groups depending on whether such a coordination is present or absent.

In the five phosphors of the first group, a change in activator concentration resolves the emission into two component bands. Their relative intensity is dependent upon activator concentration. As the concentration is lowered, the intensity of the longer wave-length band is reduced so that this band is eventually suppressed. Consequently the shorter wave band becomes the sole source of emission at sufficiently low concentration and appears as an isolated, single band. Its position is not altered by change in temperature.

With higher concentrations of activator, the intensity of both bands is reduced when the temperature is increased, but particularly that of the longer wave-length band. Owing to the increasing predominance of the shorter wave band, the peak of the longer wave band seems to be shifted to shorter wave-lengths by a tem-

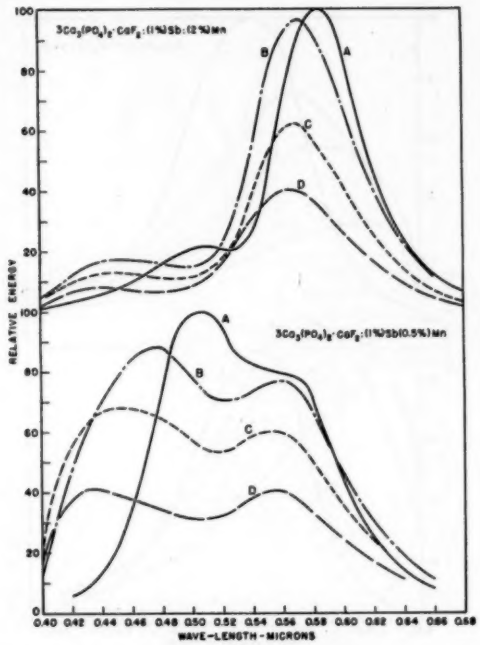


FIG. 8. Dependence of emission spectra upon temperature for calcium fluorphosphate activated with antimony and manganese. A—80°K, B—300°K, C—380°K, D—475°K.

perature rise. When allowance is made however for the extent to which the two bands overlap, it is found that the spectral position of the longer wave band as well as of the shorter actually remains unaltered on increase in temperature. At sufficiently high temperature, the longer wave band is completely suppressed, just as by reduction in activator concentration, so that the shorter wave band again becomes isolated.

TABLE I. Peak location of emission bands in calcium fluorphosphate phosphors, as dependent on activator concentration and temperature.

| | | Antimony emission at | | | | Manganese emission at | | | |
|---|---|---|---|---|---|---|---|---|---|
| % Sb | % Mn | 80° | 300° | 380° | 475°K | 80° | 300° | 380° | 475°K |
| 0.05 | 0 | 5080 | 4780 | 4600 | 4340 | | | | |
| 0.18 | 0 | 5020 | 4800 | 4600 | 4320 | | | | |
| 1.0 | 0 | 5080 | 4800 | 4550 | 4360 | | | | |
| 1.8 | 0 | 5100 | 4850 | 4700 | 4360 | | | | |
| 3.7 | 0 | 5100 | 4840 | 4670 | 4360 | | | | |
| 1.0 | 0.5 | 5060 | 4800 | 4600 | 4350 | 5800 | 5720 | 5650 | 5620 |
| 1.0 | 2.0 | 5100 | 4700 | 4600 | 4400 | 5850 | 5710 | 5700 | 5630 |
| 1.0 | 3.7 | 5100 | 4600 | 4400 | 4300 | 5850 | 5740 | 5680 | 5650 |

The interpretation of double band emission would be facilitated if two luminescence centers were involved, one for the short wave band and a separate one for the long. The basis for the distinction might lie in the degree of association of activator ions.[17] There seems however to be a difficulty in the way. The phosphorescence decay has been measured for one of these phosphors, zinc beryllium silicate. Its two emission bands, due to manganese, are well separated from one another and lie in the green and in the red. Its decay curve however shows but a single exponential rate, with no evidence that it is a composite of two different decay processes, each at a necessarily somewhat different rate. In agreement with this, its phosphorescence spectrum is identical with its fluorescence spectrum.[18]

If this should prove to be true for all cases of double band emission, it would have an important significance for the theory. It would not only denote that the two emission processes are closely related as phenomena taking place within the same activator center but it would also necessitate a revision in the conception of the mechanism responsible for them.

In contrast to these phosphors, the emission of the three phosphors in the second group cannot be resolved into component bands by change in activator concentration. An increase in temperature shifts their band to shorter wave-length. This denotes a specific effect of temperature upon the character of the excitation states.

These states may be such that the emission includes two temperature-dependent bands, closely adjacent to one another, and that an increase in temperature acts to reduce the band of longer wave-length and to intensify the band of shorter wave-length. Then an increase in temperature would be accompanied by an apparent shift of the longer wave band due to the increasing contribution made to the emission by the overlapping, shorter wave band. The effect of temperature could thereby be interpreted as altering the relation between two processes, a radiative one and a non-radiative one.

We are grateful to other members of this laboratory for the spectral distribution curves on which this paper is based. They were recorded by Gwen Lloyd under the direction of Frank J. Studer.

[17] R. V. Maurer, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948), p. 398.

[18] F. J. Studer and A. Rosenbaum, J. Opt. Soc. Am. **39**, 685 (1949).

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# The Rise in Brightness of Infra-Red Sensitive Phosphors

PETER BRAUER
*OSRAM GmbH.KG., Mosbach, Baden, Germany*
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Scott, Thompson, and Ellickson found that the rise in brightness of double activated infra-red sensitive phosphors such as SrS·Eu-Sm shows in some cases a jump, in others not. The jump and the slope of the curves of brightness *versus* time at the beginning are not proportional to the intensity of the infra-red. A model of such phosphors is described and later used to calculate the curves. The resulting equations contain both the jump and the deviation of the proportionality to the intensity of the infra-red, if the filling of traps is considered. The magnitude of the jump strongly depends on the height of a level.

SOME years ago we suggested a model[1] to explain the peculiarities of the double activated infra-red sensitive phosphors (such as SrS·Eu-Sm, SrS·Mn-Sm, etc.) which were found by us[1–6] in 1941 and to some extent in the laboratories of Siemens and Halske and later by Urbach and collaborators[7] and independently in Russia.[8] It turned out that our calculations of electronic processes based on this model gave no numerical agreement with the observed properties of these double activated phosphors. We therefore developed another model making use of the fact that the equations of the reactions of the electrons and holes are invariant when the signs of the charges are changed and further assuming that the impurity-levels resulting from the first activator are occupied levels and the impurity-levels resulting from the second activator are empty levels, as long as the phosphor is not excited. In the meantime it came to our attention that F. A. Kröger[9] had published an explanation following quite similar lines. Our investigations pointed to an energy scheme which is shown for SrS·Eu-Sm in Fig. 1 in a somewhat simplified form. This scheme, and corresponding ones for SrS·Ce-Sm, etc. which differ mainly from Fig. 1 by the height of the occupied impurity-levels, agree for the most part with the results of Urbach and collaborators. Further we found for SrS·Eu-Sm, when excited in the band around 510 mμ, only *two* maxima of the glow-curve which correspond to at least two kinds of traps. The shallow traps are caused by SrS·Eu (arrow 3) while the lower ones, also found by Urbach,[10] are caused by Sm (arrows 6–7). The arrows in Fig. 1 indicate electron transitions; arrow 1 shows the excitation mentioned, arrow 6 the stimulation, and arrow 4 the excitation of the SrS·Sm.

The presence of more than one kind of trap explains qualitatively both the inertia effects and the loss of light-sum after the beginning of the irradiation.[2,3] Scott, Thompson, and Ellickson[11] have measured recently how the brightness depends upon time. The above-mentioned model allows the calculation of their specific curves, which might be considered as a justification for the model. For the calculation we begin with an excited but no longer afterglowing phosphor, where nearly all the electrons stay in the lowest traps. The stimulating infra-red lifts the electrons to a higher level (perhaps an upper state) from where they are forwarded to the upper band thermally. Out of the upper level the electrons are now distributed among the luminescent centers, i.e., their upper states, and *all* traps. In turn the traps release electrons to the band, but nevertheless the lower ones get filled up to a considerable extent. The order of magnitude of the constants (concentrations of traps and luminescent centers, distance of levels) reasonably agrees with corresponding ideas about the crystals.

Let $N_1$ be the concentration of traps of the sort $I$ (Fig. 1), $n_I$ the concentration of the electrons trapped there, $N_{II}$ and $n_{II}$ the analog for the traps of the sort $II$, $N^+$ the concentration of the luminescent center of the dominant activator ionized by excitation. During the process of rise considered here only, the magnitude of

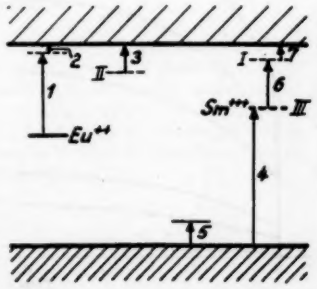


FIG. 1. Energy scheme for SrS·Eu-Sm.

[1] P. Brauer, Zeits. f. Naturforschung **2a**, 238 (1947).
[2] R. Tomaschek and P. Brauer, Zentr. wiss. Ber. Luftfahrtforsch. Nr. 1695/1 (1943).
[3] R. Tomaschek, P. Brauer, and J. Häckel, ibid. Nr. 1695/2 (1943).
[4] P. Brauer, ibid. Nr. 1695/3 (1943).
[5] P. Brauer, ibid. Nr. 1695/4 (1943).
[6] P. Brauer, Zeits. f. Naturforschung **1**, 70 (1946).
[7] F. Urbach, D. Pearlman, and W. Hemmendinger, J. Opt. Soc. Am. **36**, 372 (1946); R. T. Ellickson, J. Opt. Soc. Am. **36**, 264 (1946).
[8] W. W. Antonow-Romanowski, Ber. Akad. Wiss. UdSSR **54**, 791 (1946) [after Chem. Zentralbl. 971 (1947)].
[9] F. A. Kröger, *Some Aspects of Luminescence in Solids* (Elsevier Publishing Company, New York, 1948), p. 40.
[10] F. Urbach in "Solid Luminescent Materials," symposium held at Cornell University (1948), p. 115.
[11] F. R. Scott, R. H. Thompson, and R. T. Ellickson, J. Opt. Soc. Am. **39**, 64 (1949).

this concentration and the concentration of the occupied low sensitizer-traps (*III* in Fig. 1) are equal and so large, that their decay may be neglected. Let $z=\alpha I_{UR}$ be the number per cm³ and sec. of electrons excited by infra-red and $H=\beta N^+ n$ the brightness, $\beta$ the (summary) constant of recombination, $\delta_I$ and $\delta_{II}$ the probabilities of the transition from band to traps and $\gamma_I$ and $\gamma_{II}$ the constants for the inverse process which increase with the temperature. When quenching is not considered, the following equations are valid:

$$dn/dt=-\delta_I(N_I-n_I)n-\delta_{II}(N_{II}-n_{II})n-\beta N^+ n+\gamma_I n_I+\gamma_{II}n_{II}, \quad (1)$$

$$dn_I/dt=z+\delta_I(N_I-n_I)n-\gamma_I n_I, \quad (2)$$

$$dn_{II}/dt=\delta_{II}(N_{II}-n_{II})n-\gamma_{II}n_{II}. \quad (3)$$

When $t=0$,

$$n=n_I=n_{II}=0. \quad (4)$$

This system of equations may be solved if $n_I \ll N_I$ and $n_{II} \ll N_{II}$. Neglecting small terms we have

$$\left.\begin{aligned} n=z\Bigg[&\left(\frac{\gamma_I}{b}-\frac{\gamma_I\gamma_{II}a}{b^2}\right)\left(1-\exp\left[-\left(\frac{b}{a}-\frac{c}{b}\right)t\right]\right)\\ &+\left(-\frac{\gamma_I}{b}+\frac{\gamma_I\gamma_{II}a}{b^2}+\frac{1}{\beta N^+}\right)\left(1-\exp\left[-\frac{c}{b}t\right]\right)\Bigg],\\ \text{where}\quad & a=\delta_I N_I+\delta_{II}N_{II}+\beta N^+ +\gamma_I+\gamma_{II};\\ & b=\gamma_{II}\delta_I N_I+\gamma_I\delta_{II}N_{II}+(\gamma_I+\gamma_{II})\beta N^+;\\ & c=\gamma_I\gamma_{II}\beta N^+. \end{aligned}\right\} \quad (5)$$

Consideration of the transition in the unexcited state in Eq. (2), i.e., the inverse process to that which is represented by arrow 6 at Fig. 1, would in the first approximation change $a$, $b$, and $c$ only. Eq. (5) means: $n=z/\beta N^+$ (or the final brightness $H\sim n$) will be reached more or less gradually by an $e$-function (second term in (5)) which is modified by a compensation-process between the traps (first term in (5)).

When level $I$ approaches the upper band, $\gamma_I$ becomes very large and it follows if $t>\sim 10^{-8}$ sec.

$$n=z[1/a+(-1/a+1/\beta N^+)(1-\exp[-ct/b]), \quad (5')$$

where

$$a=b=\delta_{II}N_{II}+\beta N^+ +\gamma_{II} \quad \text{and} \quad c=\gamma_{II}\beta N^+.$$

This means that the brightness jumps to a certain value $\sim z/a$ and then reaches gradually the final brightness $\sim z/\beta N^+$. If there are two sorts (*II* and *IV*) instead of one sort we get instead (Eq. (5'))

$$\begin{aligned} n=z\Bigg[&\frac{1}{a}+\left(-\frac{1}{a}+\frac{\gamma_{II}+\gamma_{IV}}{b}-\frac{\gamma_{II}\gamma_{IV}a}{b^2}\right)\\ &\times\left(1-\exp\left[-\left(\frac{b}{a}-\frac{c}{b}\right)t\right]\right)+\left(-\frac{\gamma_{II}+\gamma_{IV}}{b}\right.\\ &\left.+\frac{\gamma_{II}\gamma_{IV}a}{b^2}+\frac{1}{\beta N^+}\right)\left((1-\exp[-ct/b])\right)\Bigg], \quad (5'') \end{aligned}$$

where

$$a=\delta_{II}N_{II}+\delta_{IV}N_{IV}+\beta N^+ +\gamma_{II}+\gamma_{IV};$$

$$b=\gamma_{IV}\delta_{II}N_{II}+\gamma_{II}\delta_{IV}N_{IV}+(\gamma_{II}+\gamma_{IV})\beta N^+;$$

$$c=\gamma_{II}\gamma_{IV}\beta N^+.$$

According to Eqs. (5), (5'), and (5'') the brightness is proportional to the intensity of the infra-red at every time. But the results of Scott, Thompson, and Ellickson show this is correct only for the final brightness ($t\to\infty$). The deviations of the proportionality point to a partial filling of the lower traps. Let $n$ be constant for a short time. Then follows from Eq. (3)

$$n_{II}=\frac{\delta_{II}N_{II}n}{\delta_{II}n+\gamma_{II}}(1-\exp[-(\delta_{II}n+\gamma_{II})t]).$$

If the process of filling comes to an end fast enough the $e$-function becomes very small and it is

$$\delta_{II}n_{II}/\delta_{II}N_{II}=1/(1+\gamma_{II}/\delta_{II}n) \quad (6)$$

or

$$\delta_{II}(N_{II}-n_{II})=\delta_{II}N_{II}[1-1/(1+\gamma_{II}/\delta_{II}n)]. \quad (6')$$

As approximation we consider the filling of the low traps by putting $(N_{II}-n_{II})$ instead of $N_{II}$ in Eqs. (5) and (5'); we obtain from (5')

$$a=b\approx\beta N^+ +\delta_{II}N_{II}[1-1/(1+\gamma_{II}/\delta_{II}n)]. \quad (7)$$

Equation (5') modified in this manner was adapted to the measurements of Scott, Thompson, and Ellickson

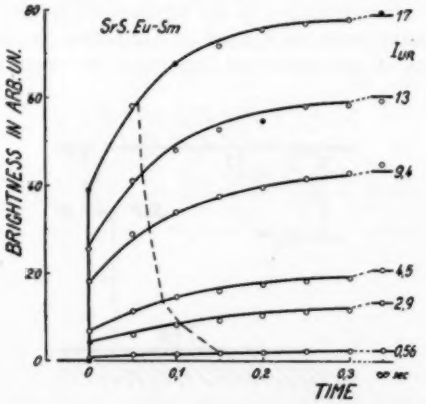


FIG. 2. Brightness vs. time for SrS·Eu-Sm when irradiated with stimulating radiation of intensity $I_{UR}$. The curves are calculated by the author, the points are taken from the paper of Scott *et al.* (see reference 11). The theoretical constants are appointed using the "filled" points.

concerning a SrS·Eu-Sm-phosphor:

$$H\sim n=n_m+(-n_m+n_{\max})\times\left(1-\exp\left[-8.7t\Big/\left(1.4-\frac{1}{1+27.3/n}\right)\right]\right) \quad (8)$$

with

$$n_m=\tfrac{1}{2}\{4.64I_{UR}-95.5+([4.64I_{UR}-95.5]^2+506I_{UR})^{\frac{1}{2}}\};\quad n_{\max}=4.64I_{UR}.$$

Equation (5) was treated quite similar using the measurements of the same authors concerning a SrSe·Eu-Sm-phosphor:

$$H\sim n=0.1905I_{UR}\left(1-\exp\left[-t\Big/\left(0.16+2.3\left[1-\frac{1}{1+1.264/n}\right]\right)\right]\right). \quad (9)$$

Figure 2 shows the rise of brightness of excited SrS·Eu-Sm irradiated with infra-red. The curves are calculated using Eq. (8), the points are taken from the paper of Scott, Thompson, and Ellickson. It should be noticed not only that a part of the final brightness is reached immediately, but further that this part is *not* proportional to the intensity $I_{UR}$ of the infra-red as it happens to be with the final brightness. Figure 3 gives the analog for SrSe·Eu-Sm using Eq. (9); it shows no sudden rise.*

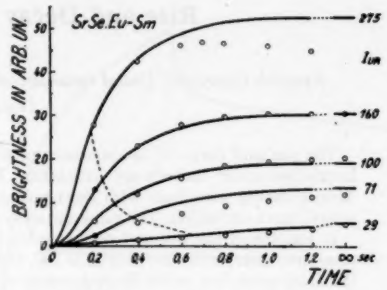


FIG. 3. As Fig. 2 for SrSe·Eu-Sm. The strong deviation of the curve $I_{UR}=275$ results from the decreasing excitation, a process not being covered by the theory. The marked deviation of curve $I_{UR}=71$ may result from an experimental error, eventually.

This phenomenon follows from our theory when the thermal transition (arrow 7 in Fig. 1) from the upper state to the band occurs rather seldom as compared to the optical transition 6. Therefore it might be expected that this type of phosphor when observed at higher temperatures will show a sudden rise of brightness too. From the theory the striking difference in the behavior of SrS·Eu-Sm and SrSe·Eu-Sm which resemble each other chemically is caused by a difference in the height of a certain level. The theory which was published recently by R. C. Herman and C. F. Meyer[12] seems to give explanation, but only for the first case.

The author is indebted to M. Schön for theoretical discussion.

* We refer to Fig. 5 of Scott *et al.* As to their Fig. 4, a small jump appears which is mentioned in the text.

[12] R. C. Herman and C. F. Meyer, J. Opt. Soc. Am. **39**, 729 (1949).

## A. G. Worthing Memorial Award

The Physics Department of the University of Pittsburgh has established the A. G. Worthing Memorial Award in honor of the late Archie G. Worthing, past president of the Optical Society of America and Professor of Physics at the University of Pittsburgh. It is to be given annually to an outstanding senior student in physics who has a record of excellent scholarship and shows promise of achievement in the future in the field of physics. This carries a cash prize of $100.00, which comes out of a fund set up by contributions made by friends of the late Dr. Worthing. The first award was made this year to William M. MacDonald at the annual Scholars Day ceremonies held by the University of Pittsburgh, April 21, 1950.

# Rise and Decay of Willemite Luminescence*

GYÖRGY GERGELY
*Research Laboratory, United Incandescent Lamp and Electrical Company, Ujpest, Budapest, Hungary*
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The rise and decay of luminescence of zinc silicate were measured at various excitation durations and intensities under cathode-ray excitation. The observed decays were displayed on a c-r oscilloscope. Measurements were made with short pulses of 1–280 microseconds separated by 20 milliseconds, and with square wave excitation. The pulse duration varied between 25 microseconds—10 milliseconds.

It was found the rise and decay curves could be separated into three components, which are strictly monomolecular, with time constants 200, 1800, and 72,000/sec. The duration of excitation does not influence the decay rates, but varies the proportions of the individual components. The fast component is predominant at very short excitation times. Using longer excitations however, the slow component gives the most part of the light emission. The same components were found with periodical excitation too. It was found that the excitation intensity does not affect the decay rates.

The brightness during the rise and decay was calculated for periodical excitation.

THIS present paper describes the investigations carried out on the phosphorescence of willemite using cathode-ray excitation of short pulses.

Measurements of this kind are indispensable for a study of the phosphorescence after a short excitation, and the details of the decay curve well under the millisecond range. The prototype of previous measuring devices was the Becquerel phosphoroscope. This ingenious apparatus however, is limited to the study of the millisecond range, its most novel forms being capable of reducing the time lag between the end of excitation and the first observation in phosphorescence to some tenth of a millisecond, but not less.[1,2]

The modern version of the present phosphoroscope was devised by De Groot,[3] who used the multiplier photo-tube, as the light sensitive element, and observed the variation of the multiplier current on the screen of a cathode-ray oscilloscope. This procedure is adapted for photographing the entire decay curve, as a cathode-ray pattern. When the heating of the phosphor is negligible, because of the excitation and change in fluorescence color, the cathode-ray pattern gives values proportional to the instantaneous phosphorescence intensity.

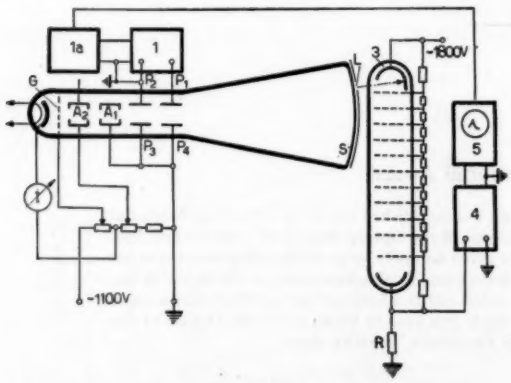



FIG. 1. Schematic diagram of the experimental arrangement.

Such measurements were performed also by Schleede and Bartels[4] and by Strange and Henderson,[5] using cathode-ray excitation. The fluorescent material to be examined has to be mounted on the screen of a c-r tube. By applying suitable pulses to the grid or the deflecting plates and placing the cathode of the photo-tube opposite the spot, the luminescence rise and decay can be observed on the screen of another oscilloscope.

Strange and Henderson have refined the idea for monomolecular processes (exponential law), having equalized the multiplier voltage with a condenser discharge of variable time-constants. By selecting the proper resistance and capacitance values, the oscilloscope pattern gave a horizontal straight line, the time-constants of the phosphorescence being equal to that of the condenser discharge.

The present investigations deal with the phosphorescence of an artificial willemite used for cathode-ray tubes. Excitation was in pulses of varying duration between 1 and 280 microseconds, separated in each case by an interval of 20 milliseconds. Measurements were carried out with an excitation of rectangular wave form, the pulse length being equal to that of the pause.

## EXPERIMENTAL METHOD

The arrangement is to be seen in Fig. 1. The pulses were produced by the pulse generator 1 applied to the deflecting plate $P_1$ of the c-r tube. Deflecting plates $P_2$, $P_3$, and $P_4$ were at ground potential with the anode $A_1$.

The deviations from the rectangular wave form during the rise and fall of the voltage were less than 0.5 microsecond. The fluorescent screen $S$ was covered

* Part of a dissertation presented to the University of Technical Sciences, Budapest, for the partial fulfillment of the requirements for the degree of Doctor of Technical Sciences.

[1] G. Fonda, J. App. Phys. **10**, 408 (1939).
[2] F. A. Kröger, Physica **14**, 81 (1948).
[3] W. De Groot, Physica **6**, 275 (1939); **7**, 432 (1940).
[4] A. Schleede and B. Bartels, Physik. Zeits. **39**, 936 (1938).
[5] J. W. Strange and S. T. Henderson, Proc. Phys. Soc. (London) **58**, 369 (1946).

with black paper, except a 2×2 sq. mm spot $L$, on which the electrons impinged during the pulse. A multiplier photo-tube 3 was placed before this spot with an anode resistance of 70,000 ohms. The signals were amplified by a two-step wide band amplifier 4/25 c-5 Mc and brought on the plates of a c-r oscilloscope,[5] the pattern of which was photographed.

The pulses were produced by a multivibrator, the square waves by a square wave generator 1, the audio-frequency generator 1$a$ controlling the former.

## PULSE EXCITATION

Measurements were made with pulses of duration 1, 3, 6, 14, 29, 36, 70, 85, and 280 microseconds. Figures 2–5 show the rise and decay of the phosphorescence. Figure 2 shows the rise and decay after 3, 6, 14, 29, 36, and 85 microsecond excitation for the same excitation intensity and a sweeping rate of about 10 kc. In Fig. 3, the first four of these curves are plotted for a sweeping rate of 50 cycles. Figure 4 presents the 29 and 280 microsecond excitation at the same intensity of excitation. The effect of varying the excitation intensity is demonstrated in Fig. 5.

In the evaluation of the data it must be kept in mind that the decay is not yet finished at the end of an excitation pause, and the amplitudes of the cathode-ray patterns are to be increased by this constant remainder.

This constant correction is determined by assuming the phosphorescence process to be a strictly monomolecular one.

$$I = I_0 e^{-\alpha t}.$$

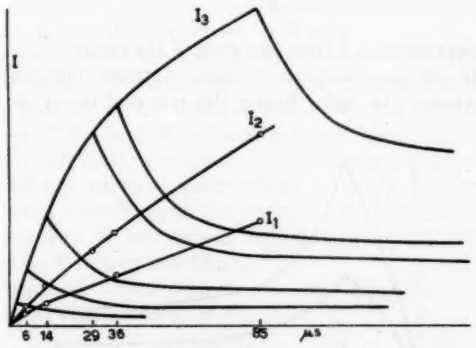



FIG. 2. The light intensity of rise and decay in arbitrary units, plotted against time. $I_1$, $I_2$, and $I_3$ are the rise curves for the three exponentials.

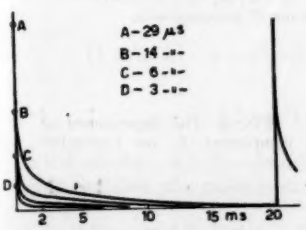



FIG. 3. The light intensity between two excitations. Intensity in arbitrary units. The rise curve is perpendicular.

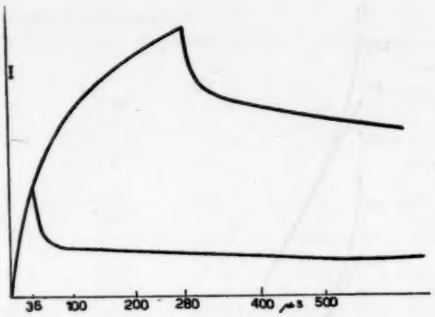



FIG. 4. The rise and decay curve for 29 and 280 microsecond excitations. Intensity in arbitrary units, ordinates the same.

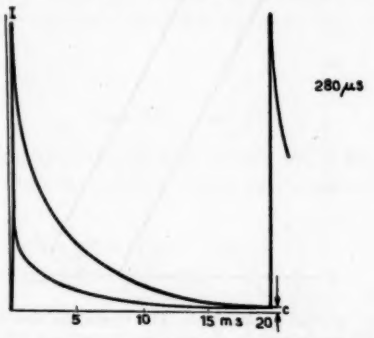



FIG. 5. The effect of varying light intensity. Excitation time 280 microseconds.

This relation plotted in the semilogarithmical plot ought to give a straight line. By choosing different values for the phosphorescence at the end of the pause this condition was fulfilled. It must be noted, that this procedure affects mostly the points at the end of the decay, the values of the first instants being almost unaffected.

This analysis gives for the greater part of the phosphorescence, notably above 3 milliseconds, an exponential law with a time-constant $\alpha_1 = 200$ sec.$^{-1}$. The remainder seems to be governed again by the same law, with the decay constant $\alpha_2 = 1800$ sec.$^{-1}$. This process is negligible beyond 3 milliseconds. Both processes still do not describe adequately the whole phosphorescence. Quite at the beginning another much shorter exponential decay is to be observed, with the constant $\alpha_3 = 72{,}000$ sec.$^{-1}$, and becoming indistinguishable after the first 30 microseconds of the decay.

That a single exponential law is unable to explain the entire phosphorescence, is demonstrated in Fig. 6, where the second process is clearly visible. In Fig. 6 the phosphorescence is shown after two excitations, each of 280 microsecond duration, but at different intensities. Figure 6 shows the proportionality of the phosphorescence with excitation, indicating a monomolecular reaction. The same is to be seen in Fig. 7 for an excitation of 29 microseconds.

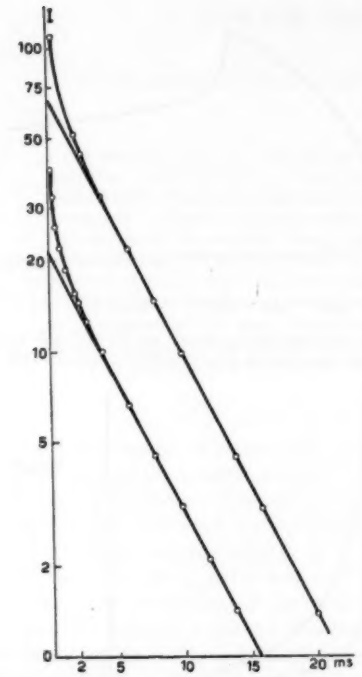



FIG. 6. Log$I$ plotted against time. The excitation time is in both cases 280 microseconds, the exciting intensity is different.

The shortest component reaches saturation very early and it does not increase appreciably beyond the excitation of 36 microseconds, as is to be seen in Fig. 8, where the magnitude of the component $I_3$, determined by the above calculations, is plotted *versus* time. The same is indicated on Fig. 4 where it is evident that the short components are about the same after 36 or 280 microsecond excitation.

The time constants $\alpha_1$, $\alpha_2$, $\alpha_3$ were nearly equal for all excitations between 3 and 280 microseconds.

The determinations of the decay constants $\alpha_1$ and $\alpha_3$ are the most reliable. The first one is responsible for the slow decay at the later stages, and can be exactly measured. The constant $\alpha_3$ gives an abrupt decay but only in the first instants, and the possible extrapolation of the other processes can affect $I_3$ but little.

These three exponentials have been found in all the willemites investigated, but the values of the decay constants depend on the manganese concentration. These investigations will be published at a later date.

Figure 2 gives information about the individual magnitudes of each of these three exponentials. Up to 15 microseconds the induction curves are nearly linear, showing that the proportions of the amplitudes are nearly constant.

At 15 microseconds the ratio is:

$$I:I_1:I_2:I_3=100:22:12:66.$$

With longer excitations the slowest process becomes more and more predominant, at 280 microseconds e.g., $I:I_3=100:25$, and at 10 milliseconds:

$$I:I_1:I_2:I_3=100:92:6:2.$$

It can be inferred therefore, that the phosphorescence of willemite consists of three processes, the first two reaching saturation very early.

Now let us calculate the dependence of the rise and decay on the time and intensity of excitation. The number of centers being $n_0$ the number of excited centers $n$ in a cm$^3$, the probability of excitation $b$, in a cm$^3$ and a second, the probability of emission $\alpha$, the excitation current intensity $i$, we have

$$dn/dt=ib(n_0-n)-\alpha n. \tag{1}$$

This after integration gives

$$n=\frac{ibn_0}{ib+\alpha}[1-e^{-(ib+\alpha)t}]. \tag{2}$$

The light intensity is proportional to $\alpha n$, so during the rise of fluorescence

$$I_r=c\frac{ib\alpha n_0}{ib+\alpha}[1-e^{-(ib+\alpha)t}]. \tag{3}$$

If the excitation is finished in time $T$, then the phosphorescent intensity is:

$$I_\alpha=c\frac{ib\alpha n_0}{ib+\alpha}[1-e^{-(ib+\alpha)t}]e^{-\alpha t}, \tag{4}$$

$t$ being measured from the start of the decay.

If the luminescence consists of three independent processes, the light during the rise and decay is the

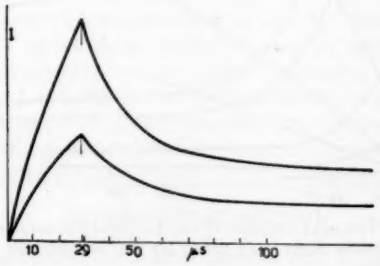



FIG. 7. The effect of varying light intensity. Excitation time 29 microseconds.

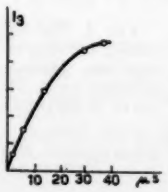



FIG. 8. The dependence of component $I_3$ on excitation time.

TABLE I. Analysis of the results by periodical excitation.[a]

| | | | | | 1 | | | | | 25 |
|---|---|---|---|---|---|---|---|---|---|---|
| (1) | $T$ | 10 | 5 | 2.5 | millisecond | 500 | 250 | 100 | 50 | microseconds |
| (2) | $\Delta I$ | 66 | 49.4 | 28.1 | 14.7 | 9.08 | 5.48 | 3.38 | 2.82 | 1.90 |
| (3) | $I_i$ | 70 | 72.5 | 73.5 | 74.5 | 75 | 75.5 | 76 | 76.5 | 77 |
| (4) | $F_1$ | 0.964 | 0.820 | 0.71 | 0.630 | 0.600 | 0.574 | 0.574 | 0.574 | 0.574 |
| (5) | $I_{e_1\text{obs.}}$ | 10.4 | 22.1 | 35.7 | 44 | 47 | 49.8 | 51.1 | 52 | 52.8 |
| (6) | $I_{e_1\text{calc.}}$ | 10.4 | 22.1 | 34 | 42.8 | | | | | |
| (7) | $F_1I_{e_1}$ | 76.4 | 66.4 | 57.5 | 5.1 | 48.6 | 46.4 | 46.4 | 46.4 | 46.4 |
| (8) | $G_1$ | 0.814 | 0.529 | 0.282 | 0.114 | 0.057 | 0.028 | 0.011 | 0.0057 | 0.0029 |
| (9) | $G_1I_{10}$ | 65.2 | 42.4 | 22.4 | 9.13 | 4.58 | 2.24 | 0.91 | 0.46 | 0.23 |
| (10) | $I_{e_1}$ | 76.4 | 65.7 | 57.8 | | | | | | |
| (11) | $F_2$ | 1 | 1 | 1 | 0.93 | 0.812 | 0.712 | 0.63 | 0.60 | 0.545 |
| (12) | $F_2I_{20}$ | 4.65 | 4.65 | 4.65 | 4.32 | 3.78 | 3.32 | 2.93 | 2.79 | 2.54 |
| (13) | $G_2$ | 1 | 1 | 0.99 | 0.772 | 0.478 | 0.256 | 0.101 | 0.054 | 0.027 |
| (14) | $G_2I_{20}$ | 4.65 | 4.65 | 4.6 | 3.58 | 2.22 | 1.24 | 0.465 | 0.251 | 0.126 |
| (15) | $\Delta I_3$ | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 1.85 | 1.44 |
| (16) | $\Sigma\Delta I_k$ | 71.85 | 49.05 | 29 | 14.71 | 8.80 | 5.48 | 3.38 | 2.82 | 1.90 |

[a] See text for notations.

total of the individual contribution. The rise rates of the processes were found to be $ib_1+\alpha_1=270$ sec.$^{-1}$, $ib_2+\alpha_2=2500$ sec.$^{-1}$, $ib_3+\alpha_3=57{,}000$ sec.$^{-1}$ this latter value being in sharp contrast to the $\alpha_3$ value of 72,000 found from the decay. This discrepancy cannot be explained by the simple monomolecular hypothesis, the situation seems to be more complicated. Difficulties were encountered by Strange and Henderson too in the interpretation of their rise curves.

## PERIODICAL EXCITATION

Measurements were performed using square wave excitation, the pauses between subsequent pulses being of the same duration as the pulse.

Pulses of 25, 50, 100, 250, 500 microseconds and of 1, 2, 5, 5, and 10 milliseconds were used.

As the interval becomes shorter between consecutive pulses, a greater portion of centers remains excited at the beginning of the next excitation, and the light increases. This increase of intensity continues, till the equilibrium state is reached. The phenomenon gives a cathode-ray pattern, which shows naturally only the change of intensity from the beginning of the excitation till the end of the decay. Such measurements were made by Williams and Eyring.[6]

They have shown that denoting the decay constant by $\alpha$, the rise constant by $\beta$ and by

$$f_m=\exp[-(t_{m+1}-t_m)\beta],\quad g_m=\exp[-(t_{m+1}-t_m)\alpha].$$

Finishing the excitation at $t=t_m$, the instantaneous light intensity is given by

$$I=c\frac{ibn_0}{ib+\alpha}(1-f_{m-1}(1-g_{m-2}\{1-f_{m-2}\cdots[1-g_1(1-f_0)]\}))e^{-\alpha(t-t_m)}. \quad (5)$$

In the present case $f_m=f$ and $g_m=g$, $t_m=T(2m-1)$, $T$ being the time of a pulse or an interval, i.e., the half-period,

$$f=e^{-\beta T},\quad g=e^{-\alpha T}.$$

Denoting by $I_k$ the intensity at the end of $k$th excitation, the quantity $(cibn_0)/(ib+\alpha)$ by $I_0$ we have

$$I_1/I_0=1-f$$
$$I_2/I_0=1-f[1-g(1-f)]=1-f+fg-f^2g$$
$$I_3/I_0=1-f\{1-g[1-f(1-g(1-f))]\}$$
$$=1-f+fg-f^2g+f^2g^2-f^3g^2 \quad (6)$$

$$\cdot$$
$$\cdot$$
$$\cdot$$

$$I_k/I_0=1-f+fg-f^2g+f^2g^2-\cdots+f^kg^{k-1}.$$

Equilibrium is reached, when

$$I/I_0=1-f+fg-f^2g+\cdots$$
$$=1-f(1-g)(1+fg+f^2g^2+\cdots)$$
$$=1-f(1-g)/(1-fg)=(1-f)/(1-fg). \quad (7)$$

This $I$ decays after a time $T$ to the value $(1-f)/(1-fg)g$.

The difference of these quantities gives the light amplitude $\Delta I$ in an interval $T$ (see Fig. 9).

$$\Delta I=I_0\frac{(1-f)(1-g)}{1-fg}. \quad (8)$$

This $\Delta I$ can be observed on the oscilloscope.

The rise and decay in equilibrium conditions obey the following relation:

$$I_r=I_0 1-e^{-\beta t}(1-g)/(1-fg)$$

$t$ being measured from the start of rise. The decay

$$I\alpha=I_0[(1-f)/(1-fg)]e^{-\alpha t}$$

being measured from the start of decay.

If one compares these expressions with the formula for a single excitation, it is seen, that the exponential is multiplied by a fraction, which tends to unity as the pulse duration increases.

[6] F. E. Williams and H. Eyring, J. Chem. Phys. 15, 289 (1947).

As already mentioned the oscilloscope pattern indicates only the difference $\Delta I$. $I_e$ was measured at long intervals with the same method, as used for the pulse excitation.

The same quantity was calculated in shorter intervals by measuring the multiplier current, being proportional in the notation of Fig. 9 with $I_m+I_e$. $I_e$ can be calculated from the rise and decay curves; $I_e$ was calculated for the 10 millisecond and 5 millisecond excitation with the same method as for the pulse excitation.

These data gave us the relation between multiplier current and oscilloscope amplitude and were used throughout the measurements.

The measurements with periodic excitation show that the components found by short duration impulses are to be distinguished here too.

$\alpha_1$ was found to be 200 sec.$^{-1}$, $\alpha_2=1800$ sec.$^{-1}$. The determination of $\alpha_3$ proved to be very difficult owing to the relatively slight amplitude of this component for long excitations, and to the little change in light intensity for short period excitations.

The constant of the rise curve $\beta$ was determined by the assumption that the $\log(I_0-I)$ *versus* time curve should be a straight line. This plot does not give a linear law by any selection of $I_0$, at the interval 0–2 milliseconds. The curve seems to run consequently higher than the straight line, very similar to Fig. 6. This can be explained by recalling the existence of the processes with decay constants $\alpha_2$ and $\alpha_3$. The plot of $\log(I_0-I)$ gave $\beta_1=270$ sec.$^{-1}$. The quantity $(1-f)/(1-fg)$ was found to be for the 10 milliseconds excitation, with $\alpha=200$ sec.$^{-1}$, $\beta=270$ sec.$^{-1}$, 0.88.

Otherwise at time $t=0$ the light intensity is $I_e$, just as at the end of the prior decay

$$I_e=I_0[1-(1-f)/(1-fg)].$$

This calculation gave 0.864 for the second term instead of 0.88.

### NOTATIONS ON TABLE I

Table I contains the results: $T$ is the duration of the excitation; $\Delta I$ is the amplitude of the oscilloscope pattern, $I_s-I_e$ in the previous notation; $I_i$ the multiplier current measured by a galvanometer. $F_1$ the fraction $(1-f_1)/(1-f_1g_1)$; $I_{e_1\text{obs}}=I_{e_1}$ the calculation of which was outlined earlier; $I_{e_1\text{calc.}}=I_{e_1}$ calculated from the straight line of $\log I$; $I_{s1}=F_1I_{10}$; $G_1$ the fraction $[(1-f_1)/(1-f_1g_1)](1-g)$; $I_{s1}-I_{e1}=G_1I_{10}$. $I_{s1}$ is calculated from the extrapolation of $\log I_1$.

The second and ninth line show the observed $I$ and the calculated $G_1I_{10}$ height of the oscilloscope pattern. There is a considerable difference between both columns and this difference can be very plausibly removed by taking in account the $I_2$ and $I_3$ processes too. For the

FIG. 9.

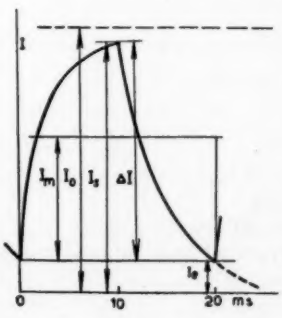



FIG. 11.

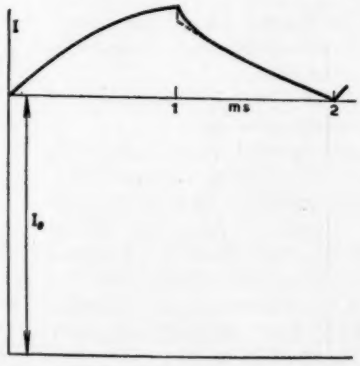
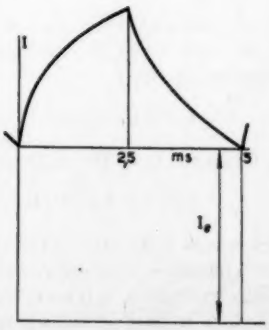
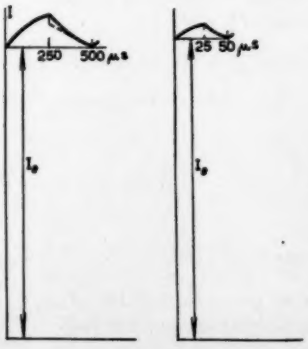



FIG. 10.




FIGS. 12 AND 13.




FIGS. 9–13. The rise and decay curve for periodical excitations. The constant part of the light denoted by $I_e$.

calculation of $I_{20}$ the excitation of 2.5 milliseconds is the best suited, for the component $I_2$ gives here the greatest contribution (Fig. 10). For the calculation of $F_2=(1-f_2)/(1-f_2g_2)$, $\alpha_2$ was made equal 1800, $\beta_2=2500$ sec.$^{-1}$. The next lines give $F_2I_{20}=I_{s2}$, $G_2=[(1-f_2)/(1-f_2g_2)](1-g_2)$ and $\Delta I_2=I_{s2}-I_{e2}$.

Besides the components $I_1$ and $I_2$ there is still some remainder; this was supposed to be caused by the component $I_3$, which was analyzed at 250 microseconds excitation; the same values were used for longer excitations because of the relative saturation of $I_3$.

The sum of these three contributions is contained in the last line, $\Sigma\Delta I_k$.

Figures 9–13 show the photographs of the oscilloscope patterns for 10, 2, 5, 1, 0.25 and 0.025 milliseconds excitation. The component $I_3$ is clearly discernible on these figures.

If the excitation frequency is increased, the value $I=I_s=I_0[(1-f)/(1-fg)]$ tends to $I_0[\beta/(\beta+\alpha)]$.

The proportion of this value to the amplitude for the equilibrium condition, $I_0$, is $[\beta/(\beta+\alpha)]$. The measurements gave for this fraction 0.66, as against the 0.575 calculated. The cause of this difference may be found partly in processes 2 and 3, partly in the trap mechanism investigated by Randall,[7] and partly because the highest excitation frequency was 20 kc.

[7] J. T. Randall and M. H. F. Wilkins, Proc. Roy. Soc. (London) A184, 347 (1945).

FIG. 14. The light intensity at the beginning of the decay plotted against cathode current. The excitation time is 10 milliseconds.

The exciting intensity was varied for the 10 milliseconds pulse. The results are to be seen on Fig. 14. At slight excitation intensities, where $ib$ is negligible in $ib+\alpha$, the light output increases linearly with $i$.

The decay constant was always 200 sec.$^{-1}$.

## CONCLUSIONS

These investigations have indicated that the phosphorescence of willemite is a complex phenomenon and cannot be accounted for entirely by the simplest monomolecular hypothesis.

These measurements have shown that the fundamental problems of phosphorescence are to be investigated well under the millisecond range and this domain is theoretically more interesting than the temperature dependent phosphorescent tail.

## Technical Publications

In general, trade publications have not been reviewed in this Journal; however, recent publications containing technical material and articles of interest to workers in the fields of optics, spectroscopy and microscopy merit notice and comment. It is understood that these are available to interested personnel without charge except as noted.

**Instrument News,** published by Perkin Elmer, Glenbrook, Connecticut. Vol. 1, No. 1 was released in the fall of 1949 and No. 2 early in 1950. The first two numbers contained articles on the use of infra-red in the drug and biochemical fields and in cold rubber research, a super Schmidt meteor camera, clincial diagonosis by electrophoresis, the need for standardization in infra-red spectrophotometry and the Harvard Observatory program in South Africa.

**Spectrographer's News Letter,** published by Applied Research Laboratories, Glendale, California. Now in its third volume of four to six page releases, it provides descriptions of new spectrographic analysis equipment and discussions of the theoretical considerations involved in equipment and analysis procedures.

**Catalog of Infra-Red Spectrograms,** issued by Samuel B. Sadler and Son, Philadelphia, Pennsylvania. A list of a collection of over 1000 spectrograms is available without cost from the publishers. The spectrograms are available by purchase either singly or as the complete collection. The spectrograms are published on cards 7 in.×18 in. with Keysort punching for sorting and selection. Additions to the series are being made.

**A New Approach to Problems Encountered in Colorimetric Absorption Analysis** by A. Rouy, published by E. Leitz, New York, New York. This is a twenty-page bulletin on a theoretical analysis of the equations involved in the presentation of absorption spectra data.

**The Educational Focus,** published by Bausch and Lomb Optical Company, Rochester, New York. A quarterly publication, it contains news notes, descriptions of new optical instruments and original articles by contributors. It is now in its twenty-first volume and is widely known and appreciated by optical workers for its interesting presentations.

# The Effects of Daylight and Tungsten Light-Adaptation on Color Perception*,†

R. W. G. HUNT
*Kodak Limited, Harrow, England*
(Received December 5, 1949)

A description is given of an apparatus which has been used to investigate how the color sensation corresponding to a given stimulus changes as the state of adaptation of the eye is altered.

A limited series of results obtained with the apparatus reveals some very striking changes in color sensation as the adaptation is varied. Most colors appear much more saturated to the light-adapted eye than to the dark-adapted eye, and changes of hue also occur. The light-adapting radiations used were the I.C.I. standard illuminants, *A* and *B*, and their effects exhibited large differences.

A few adaptation and recovery curves plotted against time are given, and indicate that photo-chemical rather than electrical processes are controlling the adaptation effects.

The saturation effect is used to deduce a picture of retinal processes in the light- and dark-adapted states, and this is summarized in Table I and Fig. 11.

A practical demonstration of the increase in saturation on light-adaptation can be seen in Fig. 12.

## INTRODUCTION

THE work of Wright[1] and of Schouten and Ornstein[2] on adaptation phenomena, using binocular matching techniques, has established quantitatively that the sensation produced in the brain by any light stimulus is a function not only of the quality and size of the stimulus but also of the state of adaptation of the retina at the time of viewing. Both workers have reported enormous changes of apparent brightness of test objects when adaptation conditions are changed, and Wright has also reported very large color changes when colored adapting radiations are used.

Evans[3] has attempted to extrapolate Wright's results in order to investigate the bearing of adaptation phenomena upon color photography. One of the problems considered by Evans was that of the effect of general adaptation or color constancy,‡ with particular reference to the differences between the effects produced by daylight and by tungsten-light adaptations. A brief résumé of the nature of this problem would probably not be out of place.

Most photographic color processes are designed so that when the three dyes are present in the concentrations necessary to give a white (or neutral) color, the result is nearly non-selective; the purpose of this being that such whites will be perceived as whites in a wide range of illuminants, owing to the effect of color constancy. Now, if the color rendering is to be faithful, whites in the original must appear as whites in the reproduction, and hence they must give rise to the particular dye concentrations which produce the non-selective result described above. But whites in the original may consist of white surfaces illuminated by daylight, artificial light, or some other type of illuminant, and hence have varying energy distributions; these are all seen as more or less white, owing to the adaptation of the eye to the illuminant, but of course the sensitivities of the photographic material are unchangeable, and hence will give different reproductions for whites under different illuminants. It is for this reason that color processes can be balanced to give a roughly non-selective white reproduction for white surfaces under only one specified illuminant. Then, if a scene is photographed when illuminated by the specified illuminant, all whites will be reproduced as approximately non-selective whites, and will therefore appear white when viewed under any type of illuminant. If any other than the specified illuminant is used to illuminate the original scene, the reproduction will appear incorrect, since the camera will have seen it when it is "adapted" to the specified illuminant, while the eye will have seen it when adapted to the actual illuminant. The position may be retrieved, as far as whites are concerned, by a compensating adaptation of the eye while viewing the reproduction, but usually the eye remains adapted to the prevailing illuminant, and hence the required compensating adaptation will not take place.

It is usually claimed that the practice of balancing the sensitivity of emulsions to specified illuminants so as to give approximately non-selective neutrals enables whites and grays to be reproduced satisfactorily. This claim might be disputed, but it is clear that even if by this method whites and grays are reproduced satisfactorily, such is not likely to be the case for colors. For a color to be reproduced correctly, it must produce in the eye adapted to the final viewing conditions a sensation equal to that produced by the original in the eye adapted to the original viewing conditions. These two states of adaptation are nearly always different

* Communication No. 1206-H from the Kodak Research Laboratories.

† From the research laboratory at Kodak Limited, Harrow, England. Read before the Colour Group of the Physical Society of London, June 9, 1948.

[1] W. D. Wright, (a) Proc. Roy. Soc. **115B**, 49 (1934); **122B**, 220 (1937). (b) J. Sci. Inst. **16**, 10 (1939). (c) *Researches on Normal and Defective Colour Vision* (Henry Kimpton, London, 1946), pp. 209–289.

[2] J. F. Schouten and L. S. Ornstein, J. Opt. Soc. Am. **29**, 168 (1939).

[3] R. M. Evans, J. Opt. Soc. Am. **33**, 579 (1943).

‡ By "color constancy" is meant the tendency of colored objects to give rise to the same color sensations when seen under illuminants of widely different color.

and in particular the original illuminant is often daylight, whereas the viewing illuminant is artificial light. It may therefore be that adaptation phenomena play a considerable part in either producing a desired effect or in preventing its being produced; thus, it was thought that an investigation into some of the effects of adaptation might either help in improving reproduction or prevent time and effort being wasted in the setting up of limits of tolerance which, in view of adaptation phenomena, might be quite inappropriate. It was decided therefore to investigate the changes of appearance of colors due to visual-adaptation phenomena, with special reference to daylight and tungsten-light illuminants.

In practice, change of illuminant, of course, brings about changes in the appearance of colored surfaces, quite apart from any adaptation effects, on account of the change in energy reflected at each wave-length from the surface. Changes in appearance accompanying changes in illuminant have therefore two aspects: first, those due to changes in the stimulus, and second, those due to change in the physiological state of the eye owing to adaptation phenomena. In the first case, the effect is non-existent for monochromatic colors, small for most very saturated colors, and most pronounced for desaturated and white colors. In the second case, the effect is probably smallest for white colors, and larger for more saturated colors.

Consideration of the two problems together is complicated by the fact that each surface and illuminant combination should really be considered separately, but some experiments have been made by Helson and Grove,[4] using Munsell patterns as samples and standard I.C.I. illuminants, $S_A$ and $S_C$. It is not clear that their observers were fully adapted to the two illuminants during the experiments, but it is shown that for some colors, a considerable change in appearance occurs, while for others almost complete color constancy exists. Their results are no doubt to be explained by the interaction of the effects due to the changes of stimulus and the changes of adaptation.

## APPARATUS USED

Following the examples of the work of Wright[1] and of Schouten and Ornstein,[2] a binocular technique was employed, as follows (see Fig. 1): The right eye of the observer was arranged to view a rectangular patch of light composed of a mixture of red, green, and blue primary beams of light, the quantities of which could be varied smoothly by the observer, thus enabling him to produce a very wide variety of colors. His left eye was arranged to view a test patch of light, the physical composition of which could be varied at will, but which was kept constant during each experiment. Surrounding this test patch of light was a large white screen illuminated by either daylight or tungsten light, according to which adaptation was being studied. With this arrangement, it was possible for the observer to compare the appearance of the test patch, as seen by the left eye, with the appearance of the mixture of the red, green, and blue primaries, as seen by the right eye. By altering the quantities of the three primaries, it was possible for the observer so to adjust them, that the comparison patch seen by the right eye was identical in appearance, both in color and brightness, with that of the test patch as seen by the left eye.

By keeping the right eye in a constant state of adaptation, for convenience, dark-adaptation, any changes in appearance of the test color due to adaptation or any other cause could be recorded in terms of the changes in the quantities of red, green, and blue light needed to produce the same sensation in the right eye. Thus, it was possible to measure both the quality and the magnitude of any change in sensation in the left eye caused by adaptation, this measurement being in terms of an equality of sensation produced in the observer's right eye.

## EXPERIMENTAL PROCEDURE

Before any series of observations was taken, a period of 15-min. dark-adaptation was allowed. With both eyes dark-adapted, the left-eye surround field being unilluminated, the observer then matched the test color as seen by the left eye, with the red, green, and blue mixture as seen by the right eye. The appearance of the fields of view during this operation is depicted in Fig. 2(b). In order to make it possible for the observer to see the two patches always nicely juxtaposed to one another, each eye was provided with four small fixation spots as shown; it was arranged that when these spots, as seen by the two eyes, were fused, the two patches were correctly positioned. Further, in order that the two eyes should remain dark-adapted during the matching, shutters were provided which only revealed the patches momentarily at intervals of a few seconds. Figure 2(a) shows the appearance when the shutters

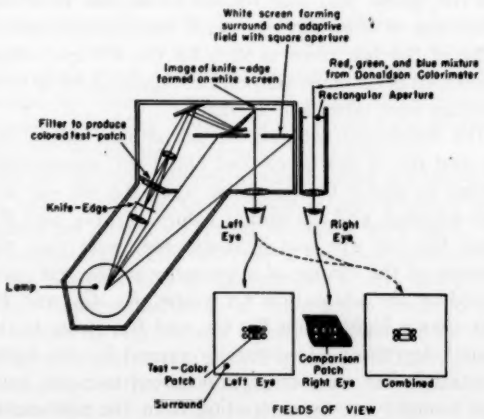



FIG. 1. Schematic diagram of the apparatus.

[4] H. Helson and J. Grove, J. Opt. Soc. Am. 37, 387 (1947).

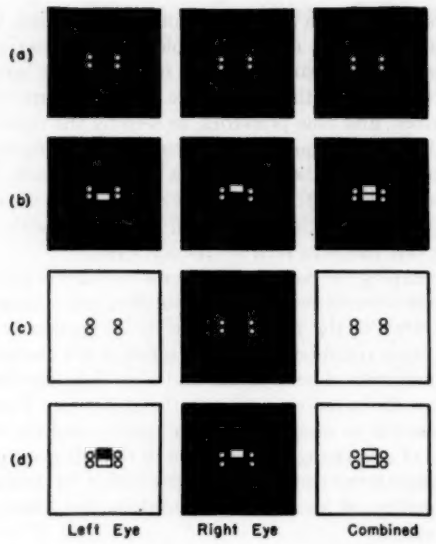



FIG. 2. Fields of view used (not to scale).

were shut. To increase accuracy, three or more of these matches were usually made in succession, and a mean value was determined.

The next step was to expose the left eye continuously for a period of 5 min. to the particular adapting radiation being investigated. (Experiments described later showed that after 5 min. the eye was completely adapted, and further adaptation produced no change in the retinal sensitivity.) During this time, the above-mentioned shutter was kept shut so that the right eye could see nothing (except the fixation spots), while the left eye saw a uniform adapting-field, with the fixation spots superimposed [Fig. 2(c)]. On opening the shutters, the test-color patch and the comparison patch could be seen [Fig. 2(d)] and compared. By opening the shutter momentarily every few seconds and adjusting the red, green, and blue control knobs, the color and brightness of the right eye patch was made to match those of the test color as seen by the left eye, under conditions of constant adaptation. Again, three or more readings were taken and averaged.

The differences between the tristimulus values, $R_D$, $G_D$, and $B_D$, of red, green, and blue light, respectively, needed to match the test color when the left eye was dark-adapted, and the similar values, $R_L$, $G_L$, and $B_L$, when the left eye was light-adapted, were then the measure of the change of appearance of the test color caused by the adaptation. Of course, $R_D$, $G_D$, and $B_D$ were always higher than $R_L$, $G_L$, and $B_L$, owing to the general depression of sensitivity caused by the light-adaptation, but color changes occurred too, and have been brought out by computing from the tristimulus values, $R_L$, $R_D$, $G_L$, $G_D$, etc., the corresponding chromaticity coordinates, $r_L$, $r_D$, $g_L$, $g_D$, etc.

$$[r_L = R_L/(R_L+G_L+B_L), \text{ etc.}$$

Hence,

$$r_L+g_L+b_L=1, \text{ etc.}]$$

Examination of these chromaticity coordinates showed that very striking chromaticity changes were taking place, and it was decided to extend the experiment to indicate whether or not this was due to simultaneous contrast. This was done as follows.

An auxiliary shutter was connected to the shutters already described, so that on opening the latter, the auxiliary shutter was closed and obstructed the light forming the adapting field. The effect was, therefore, that on opening the shutters to view the test and comparison patches, the test patch was viewed with a black surround [Fig. 2(b)], and on closing the shutters again after a moment, the surround became bright once more [Fig. 2(c)]. In this way, three matches were obtained and averaged, giving three values, $R_S$, $G_S$, and $B_S$, which represented the appearance of the test patch without the effects of simultaneous contrast. Corresponding chromaticity coordinates, $r_S$, $g_S$, and $b_S$, were also evaluated.

The above series of matches, namely, dark-adapted, light-adapted, and light-adapted without simultaneous contrast, constituted the standard experiment for each test color and each adaptation.

In addition to this, a limited number of test patches were investigated with respect to their changes in appearance with time, as adaptation and recovery processes were taking place in the retina. Initially, the dark-adapted match was made as just described. Then, during the 5-min. light-adaptation, matches were quickly made as often as possible and recorded against a stop watch. Similarly, after the 5 min. had elapsed and matches had been made with the auxiliary shutter, the adapting field was permanently removed and matches were made as often and as quickly as possible and recorded against a stop watch. In this way, it was possible to record the progress of the adaptive and recovery processes against time.

## SUMMARY OF EXPERIMENTAL CONDITIONS

### A. Right Eye

Chromaticity coordinates $(x, y, z)$ of red, green, and blue primaries:

$$\begin{aligned}\text{Red} &= 0.711x+0.289y+0.000z.\\ \text{Green} &= 0.158x+0.759y+0.083z.\\ \text{Blue} &= 0.148x+0.037y+0.815z.\end{aligned}$$

Relative luminance per scale division of primaries:

Red: 1.0. Green: 1.43. Blue: 0.067.

Size of exit pupil: 14 mm in diameter.§

§ These large exit pupils were provided to allow some freedom of movement of the observer's head while taking observations.

Approximate luminance range: 0 to 1 candle per square foot.
Size of field: 5°×2½°.

### B. Left Eye

Size of exit pupil: About 40 mm in diameter.§
Luminance of adapting field: 1.8 candles per square foot.
Luminance of test colors:

(i) Left eye light-adapted: Approx. 2.3 candles per square foot.
(ii) Left eye dark-adapted: Approx. 0.7 candle per square foot.

Size of test-color field: 5°×2½°.
Size of adapting field: 60°×60°.
Quality of adapting stimuli used:

(a) I.C.I. standard illuminant *A* (referred to as $S_A$).
(b) I.C.I. standard illuminant *B* (referred to as $S_B$). (Obtained with Chance OB5 glass filters.)

The luminance of the test-color patches was made slightly higher than that of the adapting field, since this was found to be the most favorable condition for accurate color-matching. The most common practical case corresponds with the test-color patch and adapting field having equal luminances, since under ordinary conditions of vision the adapting field will have a luminance which is the mean of those of the objects composing the field of vision. As the test patch was only 30 percent higher in luminance than the adapting field, it is considered that the practical case was approximated closely enough.

The maximum luminance obtainable in the right-eye beam was only about 1 candle per square foot, and, therefore, when the left eye was dark-adapted, it was necessary to insert a neutral-density filter into the test-color beam in order to keep its luminosity within the range of that of the right-eye comparison patch. Thus, when the left eye was light-adapted, the luminance of the test colors was about 2.3 candles per square foot, but when the left eye was dark-adapted, its luminance was only about 0.7 candle per square foot. This again corresponds roughly with practical conditions of vision, since it meant that the sensations corresponding to colors seen under different conditions of adaptation were compared at approximately equal subjective brightnesses, which tends to be the case for ordinary vision.

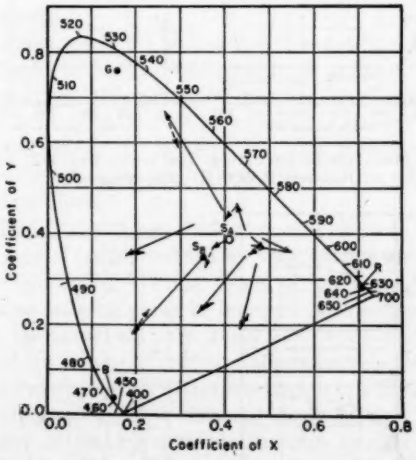



FIG. 3. Movement of colors from their dark-adapted positions under the influence of $S_A$ adaptation with surround. (Broken arrows indicate reduction of the effect caused by eliminating simultaneous contrast.)

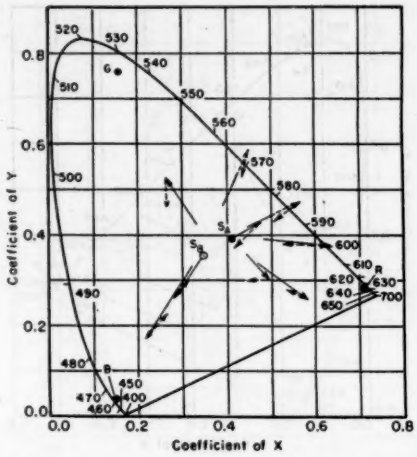



FIG. 4. Movement of colors from their dark-adapted positions under the influence of $S_B$ adaptation with surround. (Broken arrows indicate reduction of the effect caused by eliminating simultaneous contrast and are also used to indicate estimated movements outside the triangle, *RGB*.)

## RESULTS

In work of this kind there is an unavoidably large number of variables, and therefore the results so far obtained are rather restricted. For this reason, attention has so far been concentrated on chromaticity changes rather than upon brightness changes, and it may be pointed out that the nature and extent of brightness changes have been already fairly extensively investigated by, for example, Schouten and Ornstein.[2]

By far the most prominent effect found in this work has been a very marked increase of saturation in the appearance of test colors on changing from dark- to light-adaptation. This increase is subjectively obvious to the observer and in many cases is very startling. A practical demonstration of the effect is provided for the reader in Fig. 12, and incidentally shows that the difference of saturation occurs between different parts of the same retina as well as between the retinas of the two eyes.

The results obtained for 11 test colors are shown in

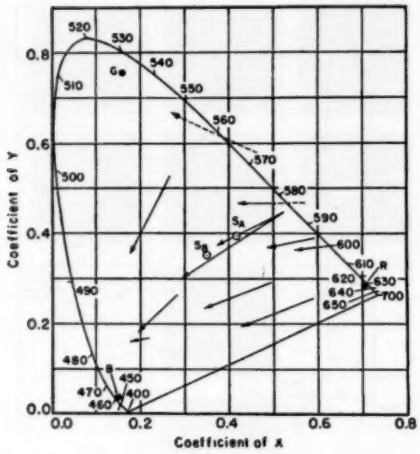



FIG. 5. Diagram showing changes of appearance of colors caused by change of adaptation from daylight, $S_B$, to tungsten light, $S_A$, the energy distributions of the colors being kept constant.

Figs. 3 and 4, where values of $r_L$, $g_L$, and $r_D$, $g_D$, transformed to the standard I.C.I. color triangle,|| are plotted for $S_A$ and $S_B$ adaptation. The full arrows join the points $(r_L, g_L)$ and $(r_D, g_D)$, and therefore indicate the changes in appearance which the various test colors undergo, on account of light-adaptation.

The magnitude of the effect is illustrated by the pale pink color at $x=0.465$, $y=0.340$, which becomes, under the influence of $S_B$ adaptation, a strong magenta at $x=0.585$, $y=0.255$, which is a change of purity from

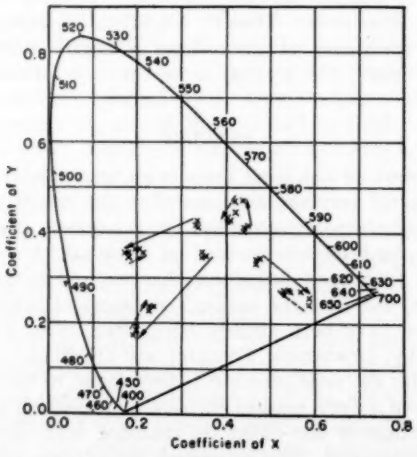



FIG. 6. Typical variations of three successive color-matches, indicating the precision of the measurements.

|| In Figs. 3 and 4, $S_A$ is plotted at an apparently incorrect position. This is due to differences between the color-vision characteristics of the author and those of the I.C.I. standard observer. All the points in these figures are liable to small discrepancies of this type, except the points, *R*, *G*, *B*, and $S_B$ (representing the three Donaldson Colorimeter primaries and the standard illuminant, *B*), which are correct.

34 to 78 percent. It was also found that many colors became so saturated upon light-adaptation that they fell outside the *RGB* triangle altogether. There was no way of measuring the exact location of such colors, but arrows have been inserted in the figures to indicate their approximate position.

The trend of the results in the figures suggests, furthermore, that if test colors near the borders of the *RGB* triangle were used, they would move right outside the dark-adapted spectrum locus altogether. This was confirmed subjectively; a saturated yellow, for instance, lying on the line, *RG*, and hence very nearly upon the spectrum locus, became still more saturated. Hence, it is concluded that the sensations which can be produced in a dark-adapted eye are only a proportion of those which can be produced in a light-adapted eye.

The results of the observations made with the auxiliary shutter are shown by the broken arrows in Figs. 3 and 4; these show the reduction of the effects of light-adaptation which is brought about by eliminating the effects of simultaneous contrast. It is seen that the reduction is too small for the effects to be due mainly to simultaneous contrast. There is a tendency for the reduction to be greater for orange and yellow colors than for others.

It will be noted that although every color shows an increase of saturation, some colors show a considerable change of hue as well.

The effects produced by the two adaptations, to tungsten light, $S_A$, and to daylight, $S_B$, are never the

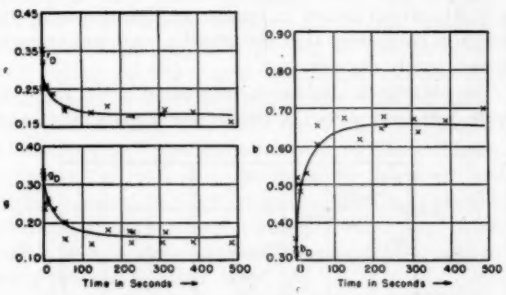



FIG. 7. Mean adaptation curves. Test color: $x=0.442$; $y=0.357$. Observer: R.W.G.H. Adaptation: $S_A$.

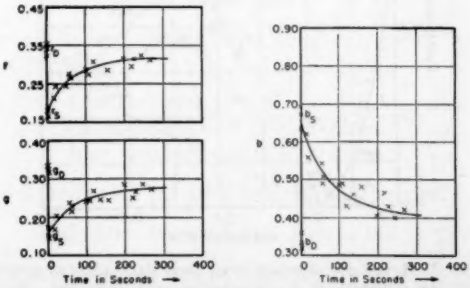



FIG. 8. Mean recovery curves. Test color, observer, and adaptation same as for Fig. 7.

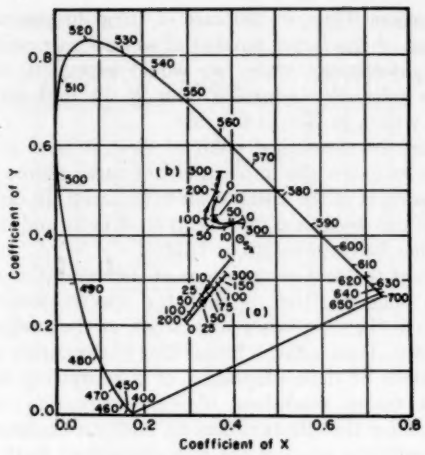



FIG. 9. Mean adaptation and recovery chromaticity tracks. Test colors: (a) $x=0.398$; $y=0.351$. (b) $x=0.425$; $y=0.435$. Observer: R.W.G.H. Adaptation: $S_A$.

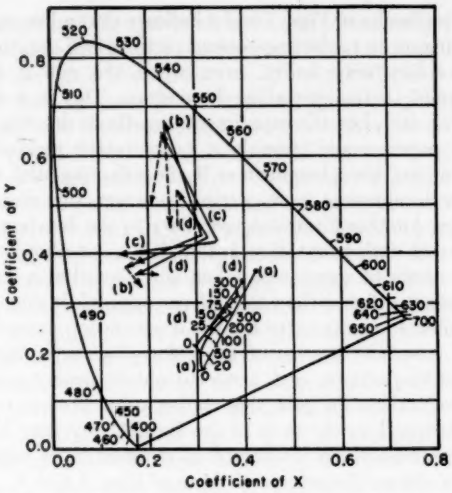



FIG. 10. Variation among observers: (a) W.D.W.; (b) L.C.T.; (c) A.M.; (d) R.W.G.H.

same and usually show differences of both hue and saturation which can be of considerable magnitude. These differences are shown in detail in Fig. 5, where the arrows show the change in appearance of a test color when the adaptation is changed from $S_B$ to $S_A$. It is seen that all colors appear bluer under $S_A$, which is to be expected, on account of a greater depression of sensitivity of the red and green receptors under the influence of that adaptation than would occur with $S_B$. In practice, of course, for most surface colors, this increased blueness in appearance is reduced, on account of the yellowing of the stimuli when the illuminant is changed from $S_B$ to $S_A$. Generalization of the results of Figs. 3 and 4 to cover the whole color triangle would enable the actual change of appearance of any surface color to be computed if its spectral-reflectance curve were known.

An indication of the accuracy with which these results have been obtained for one observer is given in Fig. 6. In this figure, the individual matches which were obtained have been plotted as crosses for several representative colors. It is seen that the spread of the observations is quite small compared with the effects of the adaptations.

In Figs. 7 and 8, mean adaptive and recovery curves of $r$, $g$, and $b$ are plotted against time for one test color, the results being kept in terms of the instrumental primaries as being easier to interpret in this case. Once again, the actual matches which were made have been marked by crosses to indicate approximately the consistency of the results. The results shown in Figs. 7 and 8 were obtained on three different days. In view of the difficulty of making accurate matches quickly under changing conditions, the results may be considered to be in satisfactory agreement. These observations are especially difficult to make during the first 25 sec., when the appearance of the test color is changing rapidly.

In Fig. 9, the results of Figs. 7 and 8 are plotted in the I.C.I. chromaticity chart (curves *a*), a time scale being marked in seconds along the track of the color changes. Figure 9 also shows the tracks of a yellow color (curves *b*) and is included to show that these tracks are not usually straight, presumably owing to the different receptor mechanisms recovering at different rates. These results resemble those obtained by Wright, in that changes occur rapidly during the first 25 or 50 sec., and then more slowly for the next 100 or 200 sec. This suggests photo-chemical rather than electrical processes.

Figure 10 gives an indication of the variations of the effects among observers. With due regard to the nature of the experiment and to the known variations of color vision among individuals, it is considered that the figure shows quite good agreement among the observers so far tested. Apart from these few results shown in Fig. 10, all the results described in this paper have been obtained by the author.

## DISCUSSION OF RESULTS

From the practical point of view, it is evident from Fig. 5 that differences in the state of the eye when adapted to standard illuminants, $S_A$ and $S_B$, result in large differences in the sensations produced by any given physical stimulus. It is true that for surface colors these differences will be reduced in practice by the compensating effect of the modification of the physical stimulus by the change of illuminant, but it is of course by no means the case that the two effects will always cancel out. Thus, it would appear to be necessary to allow for any adaptation effects when seeking correct color reproduction.

The results of Figs. 3 and 4 indicate that a low screen luminance in projecting colored pictures will desaturate the colors very badly, even when the eye is fully adapted to the prevailing luminance. This is a well-known fact, but the experimental methods described in this paper would provide a quantitative method of examining the phenomenon if the adapting and test-color luminances were varied to cover the required range. Another interesting corollary to the desaturating effect of dark-adaptation is that if a color photograph of a dimly lit scene were taken and viewed at a screen luminance higher than that of the original, it might be possible to compensate for the desaturation caused by the sensitivity curves of the color process having no negative portions, and hence to obtain nearly correct reproduction. To gain this end, a color process could be designed on the basis of the Ives, Abney, and Yule[5] compromise which desaturates all chromaticities radially in directions the reverse of those of Figs. 3 and 4.

The results also suggest that there is considerable danger in applying the findings of dark-adaptation colorimetry to subjective problems under conditions of light-adaptation, since sensations are evidently functions not only of physical stimulus but also of state of adaptation. Thus, in the case of color discrimination, because of the larger number of sensations possible in the light-adapted state, we would expect to find a higher color discrimination than in the dark-adapted state, which, in fact, is the case.

TABLE I. Summary of experimental facts and theoretical deductions.

| Facts | Deductions |
|---|---|
| 1. Monocular matches remain valid for a very wide range of states of adaptation. | 1. (a) Shapes of the fundamental sensitivity curves are constant, apart from over-all changes by a factor independent of wave-length.<br>(b) Only three independent sensitivity curves are probable. |
| 2. On dark-adaptation, all colors are desaturated. | 2. Simple variations of over-all spectral sensitivities cannot explain this. Interlinkage of the responses could explain it. |
| 3. Spectral yellow to the dark-adapted eye appears desaturated. | 3. It is the dark-adapted sensations which are desaturated, not the light-adapted, which are supersaturated. |
| 4. Nerve paths from the retinal receptors intermingle with one another. | 4. This is probably the physiological channel by which the desaturating effects take place. |
| 5. With dark-adaptation, resolving power decreases and sensitivity increases. Product of threshold intensity and area is constant for dark-adaptation. | 5. Intermingling channels are in greater use in dark-adaptation than in light-adaptation. |
| 6. Adaptation and recovery processes take place relatively slowly. | 6. Extent of the intermingling is chemically controlled. |

From the theoretical point of view, it is of interest to try to follow the implications of these results upon our concepts of the visual color mechanism. In order to clarify the discussion, a collection of facts and deductions has been drawn up in Table I.

One of the first explanations of the saturation effect which suggests itself is that the spectral-sensitivity curves of the receptors change shape as the adaptation is altered. Thus, either a broadening of the curves under conditions of dark-adaptation or a narrowing of the curves under conditions of light-adaptation would account for the effects observed. Such an explanation, however, runs afoul of the well-established fact[6] that, broadly speaking, a monocular color-match between two stimuli of widely different spectral composition remains a match under widely different conditions of adaptation. Admittedly, violations of this concept have been reported,[7] but it seems safe to say that these are exceptions due, for instance, to working at exceptionally high levels of luminance. From this fact the deduction is usually made that the shapes of the wave-length sensitivity curves of the receptors are not altered by adaptation except by an over-all factor independent of the wave-length.

If the color vision of the retina is based on a three-receptor mechanism, it is clear that simple changes in the over-all responses relative to one another could never result in all colors becoming more saturated, as shown in Figs. 3 and 4; it could only result in all the colors becoming, say, less blue, or more red, etc. Granit's work has, however, suggested that there may be more than three receptor mechanisms, and, in particular, that there may be a "white"-sensitive receptor, or *Dominator*, in addition to other selectively sensitive receptors, or *Modulators*. The adoption of such a hypothesis results in a simple explanation of the saturation effect by supposing that, at high levels of adaptation, the *Dominators* are less active than the *Modulators*, with the result that saturated sensations are obtained, whereas at low levels of adaptation, the converse is the case, resulting in desaturated sensations. Another alternative is that the same effects may be provided by the rods of the retina. These arguments depend for their success upon the existence of at least four independent receptors, but, in view of the great value of the trichromatic theory in explaining three-color matching, it is of importance to see whether the experimental facts cannot after all be explained in terms of three receptors only.

One explanation which suggests itself is that the three responses emanating from the receptors might

[5] In D. L. MacAdam, J. Opt. Soc. Am. **28**, 414 (1938).

[6] Reference 1 (c), p. 367.

[7] H. Hartridge, Nature **160**, 538 (1947).

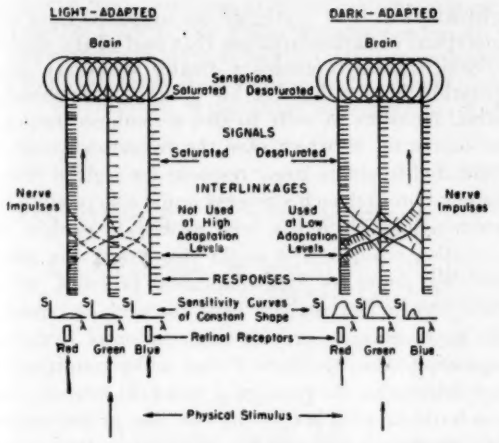



FIG. 11. Process proposed to explain decrease in saturation of the sensations produced by the dark-adapted eye.

interfere with one another at some point between the receptors and the brain. Thus, for instance, when looking at a red stimulus under conditions of light-adaptation, one might suppose that the response from the red receptor mechanism, being greater than those from the green and blue mechanisms, would tend to inhibit these smaller responses and hence give a super-saturated sensation. Conversely, under conditions of dark-adaptation, the responses might be supposed to exhibit no such inhibiting effect and hence produce sensations which by comparison are desaturated. In this case, monocular matches would always remain matches, no matter how the adaptation was altered. For, assuming that any change in adaptation would affect only the over-all sensitivity of the three receptors and not their spectral sensitivities, the three retinal responses corresponding to each half of the matching field would be affected by equal amounts, and hence if they were equal before, they would still be equal after a change in adaptation. Then the inhibitory effect being a function of the responses, and not of the physical stimuli, would mean that any modification of the final signals to the brain would affect equally those from both halves of the matching field, and hence continue to give equal sensations.

This conception certainly meets all the facts so far considered, but it requires modification, in view of the fact that yellow stimuli on or near the spectral locus become much more saturated in appearance on light-adaptation. For, it seems fairly certain that the spectral-absorption curve of the photo-chemical substance most sensitive to the shorter wave-lengths, usually referred to as the blue or violet substance, drops almost entirely to zero at wave-lengths greater than about 0.55$\mu$. The evidence for this is the straightness of the spectral locus from 0.55 to 0.70$\mu$ in chromaticity diagrams, and the shapes of the fundamental sensitivity curves derived by most observers. It might be supposed that the blue mechanism of the eye contains not only blue substance, but also some red and some green substance; but there is no evidence that this is so. Consequently, it seems reasonable to assume that a yellow stimulus gives rise to only two responses which we may suppose to be red and green. Thus, any inhibition effects could consist only of changes of hue, due to suppression of either the red or the green responses, and could not consist of changes in saturation. But, upon light-adaptation, spectral yellows definitely become more yellow in appearance, not yellow-green, or orange. It is therefore concluded that the increased saturation of colors seen by the light-adapted eye is not due to any inhibition of the weaker by the stronger responses.

However, an inversion of the hypothesis will fit all the facts. If the normal sensation corresponding to any given stimulus is regarded as the saturated one which occurs under light-adapted conditions, we may suppose that when the eye is dark-adapted the three responses tend to react so as to decrease the differences between them, and thus desaturate the corresponding sensations. Thus, when the eye is light-adapted, a spectral yellow may produce equal red and green signals, but no blue signal, while when the eye is dark-adapted, it produces red and green signals and some blue signal as well, and hence a desaturated sensation results.

In order to summarize and clarify the model which, it is suggested, fits in with the facts, a schematic diagram has been produced in Fig. 11. The left half of the diagram depicts the light-adapted state of affairs, while

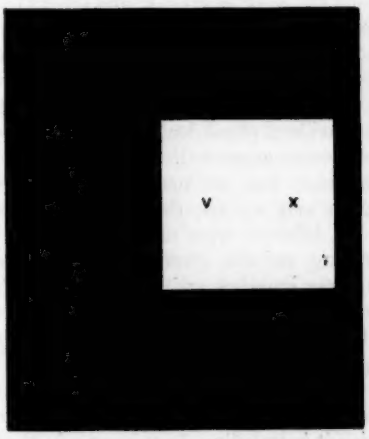



FIG. 12. To see the saturating effect of light-adaptation: Gaze at the "V" for 30 sec., and then look quickly at the "X," at the same time placing a colored filter in front of the eye, for 5 sec. Then, gaze at the V again for 15 sec. and back to X for 5 sec. Repeat procedure for as long as desired. While viewing X, keep the unfiltered eye closed.

When looking at X, left-hand side of white square is seen by a relatively dark-adapted part of the retina, while right-hand side is seen by a light-adapted part. The right-hand part will appear more saturated than the left. The effect is more prominent for some colors than for others, e.g., a saturated magenta usually gives a prominent result.

the right half depicts the dark-adapted. It is supposed that two physical stimuli, reddish in color, of identical spectral distribution but of different total energies, $E_\lambda$ and $e_\lambda$, fall on the eye, and that their magnitudes are roughly inversely proportional to the degree of adaptation, so that they appear of roughly equal brightness. The receptors of the light-adapted eye will have relatively low spectral-sensitivity curves and those of the dark-adapted eye relatively high ones; the corresponding curves, however, have identical shapes, thus maintaining monocular matches. The three receptors produce their responses in each case, which are of the same order of magnitude as shown. In the case of the light-adapted eye, these three responses give rise directly to three signals to the brain which give a sensation which is not desaturated. In the case of the dark-adapted eye, however, the responses do not give three signals directly, but there is first a spilling over of the greatest response into the other two channels, or an induction of additional responses in the other two channels. These modified responses result in modified signals reaching the brain, and hence a desaturated sensation is experienced. Figure 11 also suggests that the extent of the intermingling must be controlled by some chemical process, since the responses in the light- and dark-adapted cases are similar and only the magnitudes of the sensitivity curves vary. This is also suggested by the relatively slow nature of the adaptation and recovery curves of Figs. 7 and 8.

Is there any physiological or visual support for such a picture of the retinal and cerebral processes? It is known from the work of Polyak[8] and others that a one-to-one connection between a receptor and a nerve fiber is the exception rather than the rule, and the arborization between the receptors and the bipolar cells, and between the bipolar cells and the ganglion cells, would seem to provide a physiological basis for the spilling over of responses suggested. Moreover, since it seems to be the case that all nerve impulses are almost identical, one may suppose that the brain distinguishes between the different types of sensation, such as heat, touch, hearing, redness, greenness, etc., by the points at which these impulses arrive at the brain. Thus, if, for instance, part of the red response did spill over into a nerve fiber connected predominantly to green-sensitive receptors, the result would be to increase the green response in the brain, the identity of the red response being maintained solely by the particular nerve fiber along which it is traveling. In this way, in the example of Fig. 11, the parts of the original red response which spilled over into the green and blue nerve fibers result in a loss of red sensation, and gains in green and blue sensations, and hence the red is desaturated.

It remains to ask why this spilling over, or induction, should occur in the dark-adapted state, but not in the light-adapted. Now, Lythgoe[9] has suggested from considerations of dark-adaptation that part of the method by which the eye obtains a greater sensitivity when operating in dim light is for groups of neighboring retinal receptors to unite to give a combined response for that area, in which case the responses would be summated to give a larger response for a given retinal illumination. But such a process would also produce the intermingling which has been evoked to explain the saturation changes, and would also reduce the visual resolving power as dark-adaptation proceeds, which effect does, in fact, occur.[10] Thus, the work described in this paper seems to provide confirmation of Lythgoe's suggestion. Also, the fact[11,12] that under conditions of dark-adaptation the product of threshold intensity and area is constant fits in with the view that at low adaptations there is an intermingling of responses from neighboring retinal areas.

## CONCLUSIONS

The limited results of the work so far carried out confirm that the binocular matching method is a powerful tool for investigating differences of perception in various states of adaptation, and that, in the cases of dark, daylight, and tungsten-light adaptations, large differences occur. For a proper understanding of the phenomena, the effects on colors over the whole color triangle should be examined, and the work should be extended to indicate the effects of working with different adapting luminances, and with different test-color luminances and field sizes. It is intended to extend the work in these directions in due course.

The marked changes of saturation which occur on altering the adaptation conditions seem to lead to an explanation in terms of the spilling over of responses of one color into responses of another color, and this fits in with other visual and physiological phenomena. It must be remembered, however, that these conclusions are based, as yet, on observations over only a very limited range of luminance.

## ACKNOWLEDGMENTS

The experimental work was carried out at Imperial College, London, for Kodak Limited, and the facilities thus provided are gratefully acknowledged.

The author wishes to express his great gratitude and indebtedness to Dr. W. D. Wright, of Imperial College, for his most helpful advice and guidance during the course of this work, without which little progress would

[8] S. L. Polyak, *The Retina* (University of Chicago Press, Chicago, 1941).

[9] R. J. Lythgoe, Brit. J. Ophthalmol. **24**, 40 (1940).

[10] R. J. Lythgoe, Medical Res. Council Spec. Rep. Ser. No. 173, London (1932).

[11] C. H. Graham and R. Margaria, Am. J. Physiol. **113**, 299 (1935).

[12] H. W. Karn, J. Gen. Psychol. **14**, 360 (1936).

have been made, and also to Miss G. M. Frowde, also of Imperial College, who kindly recorded the results.

The contents of the later part of this paper are largely the results of many discussions with Dr. Wright; with Dr. L. C. Thomson, of the Vision Research Unit of the Medical Research Council; with Mr. E. R. Davies, and Mr. A. Marriage, of the Kodak Research Laboratories, Harrow; and with my father, Col. F. R. W. Hunt, of Vickers Armstrong Limited, to all of whom I am most grateful for their interest and cooperation.

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JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 40, NUMBER 6 JUNE, 1950

# A Comparison of Visual and Photoelectric Measurements of the Attenuation of Brightness Contrast by the Atmosphere*

HOWARD S. COLEMAN AND HAROLD E. ROSENBERGER
*The Optical Research Laboratory, The University of Texas, Austin, Texas*

(Received January 3, 1950)

A comparison has been made of visual and photoelectric measurements of the attenuation of brightness contrast by the atmosphere. The comparison is being made to attempt to gain an insight into the reasons for the apparently great scatter of atmospheric attenuation data obtained by early investigators in this field. In particular it is of interest to determine whether or not the lack of consistency of the early attenuation data may be attributed to unusual atmospheric conditions or to poor experimental design. The results of the comparison indicate excellent agreement between the atmospheric data obtained by the two methods mentioned. It is concluded that if proper experimental techniques are followed, there is no reason to expect visual photometry to lead to different atmospheric attenuation data than those obtained by photographic and by photoelectric processes.

## INTRODUCTION

IT is the purpose of the material presented in this paper to determine whether or not the great scatter in atmospheric attenuation data, reported in the literature by the early investigators[1] in this field, can be attributed to the use of visual photometry. Because of the excellent facilities established by the ONR at The University of Texas[2] for measuring the attenuation of brightness contrast by photoelectric processes, it was felt that if it could be shown that visual photometric measurements of the attenuation of brightness contrast by the atmosphere were in close agreement with data obtained under the same conditions using photoelectric equipment, the scattering of the early results could then likely be attributed to imperfect experimental designs rather than some inherent limitation imposed by visual photometry. In a similar connection, it has been shown that photographic and photoelectric measurements of atmospheric attenuation of brightness contrast are in close agreement.[3]

## APPARATUS AND PROCEDURE

The apparatus and procedure used at the ONR field facility at The University of Texas has been described in a previous paper[2] and consequently will not be redescribed in detail here. Only the additions to the equipment previously described will be discussed. The

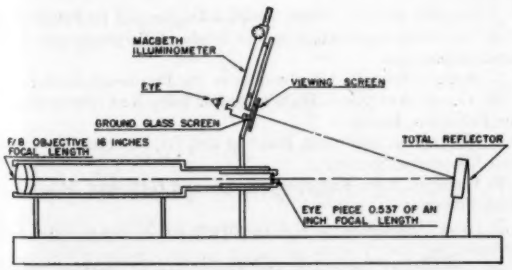


FIG. 1. Schematic diagram of visual telephotometer.

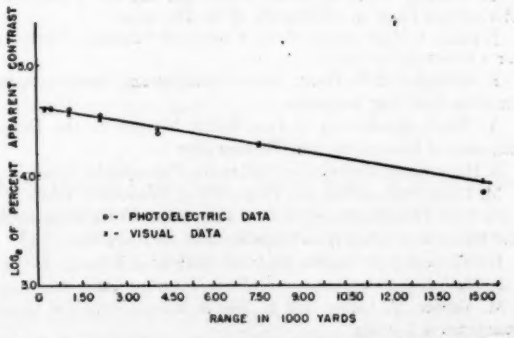


FIG. 2. A comparison of visual and photoelectric atmospheric attenuation data.

* The work described in this paper was performed, in part, under terms of Task IX of Contract N6onr-266 between the ONR of the Navy Department and The University of Texas.

[1] H. Koschmieder, Beitr. z. Phys. d. Freien Atm. **12**, 33 (1924); 171 (1925).

[2] Coleman, Morris, Rosenberger, and Walker, J. Opt. Soc. Am. **39**, 515 (1949).

[3] H. S. Coleman and H. E. Rosenberger, J. Opt. Soc. Am. **39**, 990 (1949).

apparatus used consists essentially of two telephotometers and a set of seven black and seven white visibility targets subtending the same angle (1.86 minutes) with respect to the telephotometers and located at ranges of 300 to 15,267 yards from the point of observation. One telephotometer uses a photoelectric tube and has been described in detail in an earlier paper.[2] The other telephometer utilizes the human eye as a photosensitive receptor and is shown schematically in Fig. 1.

The procedure consisted simply of making brightness measurements of the visibility targets using the two telephotometers. The photoelectric measurements were made first and immediately thereafter (within a period of one minute) visual brightness measurements were made of each of the visibility targets and the sky background against which they were viewed. It required approximately five minutes to make each set of measurements. A sample of data thus obtained is shown in Fig. 2. Approximately one hundred sets of such data were obtained.

## THE DATA

The data obtained in this study were presented as logarithmic plots of the apparent contrast as a function of range. Since all of the plots were similar, only one is presented as a sample. The more nearly the data thus plotted fall on a straight line, the more nearly is the attenuation a simple exponential function. In the sample of data presented, the straight line shown is drawn through the data obtained photoelectrically, without regard to the data obtained visually.

## DISCUSSION AND CONCLUSIONS

It is evident from the data presented in this paper, that the visual and photoelectric photometric measurements of the attenuation of brightness contrast by the atmosphere are in close agreement. For this reason there is little doubt as to whether or not visual photometry should yield the same results as photoelectric methods. This tends to indicate that the early experiments conducted in measuring the attenuation of brightness contrast using visual methods were not properly designed. For example, it may be necessary to use targets subtending the same angle with respect to the point of observation, to have reasonably rigid measuring equipment, and to reduce stray light to a minimum. It is improbable that all of these conditions were observed simultaneously by the early investigators in this field. In this connection, it is highly doubtful if the scatter in the atmospheric attenuation data reported in the literature by the early investigators could be attributed to actual atmospheric variations since relatively short ranges were involved and great care was taken to obtain data only on those few days out of the year in which similar atmospheric conditions existed. This suggests that if scientific data of laboratory precision are to be collected pertaining to atmospheric attenuation of brightness contrast, the design of the field experiments must be as carefully controlled as in the laboratory. If this is done, it is evident that visual measurements can be expected to produce essentially the same attenuation data as photoelectric measurements.

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**Proceedings of the Eleventh Congress of the Groupement pour l'Avancement des Méthodes d'Analyse Spectrographique des Produits Métallurgiques (held January 25–27, 1949, Laboratoire Central de l'Armement, Paris, France).**

J. Dickens and R. Petit: Quantitative Spectrographic Analysis of Antifriction Alloys with Rotating Electrodes

G. Brucelle: Study of Source Discharges and the Dependence of Emission Lines on the Nature of the Discharge

J. Roig: A Modification of the Wadsworth Stigmatic Mounting for a Concave Grating

P. Coheur and A. Hans: Direct Reading and Spectrographic Analysis with One Apparatus

A. Hans: Application of Line-Width Method to the Determination of Electrolytic and Thermic Zinc

A. Hans: Some Methods for Calibrating Photographic Emulsions

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# The Colors of Distant Objects*,†

W. E. KNOWLES MIDDLETON
*Division of Physics, National Research Council, Ottawa, Canada*
(Received February 23, 1950)

A general expression is developed for the apparent color of an object of any intrinsic color, seen through a given thickness of an atmosphere of any specified optical properties. In deriving this expression, the author has made use of modern theories of the alteration of contrast by the atmosphere. Some examples of the application of this theory are given, and in conclusion it is shown that the visual range of colored objects differs little from that of achromatic objects of the same luminance factor.

## 1. INTRODUCTION

IN 1935 the writer presented a theory of the apparent colors of distant objects and the visual range of colored objects.[1] While there is no reason to doubt the essential correctness of that theory, its scope was somewhat limited by the state of the theory of the visual range at that time; and as this has been greatly refined as a result of researches carried out during the Second Great War, it is now possible to set down a theory of the apparent colors of distant objects which is at once more general and more concise than it could have been fifteen years ago.

It will be assumed that the reader is acquainted with, or has access to, the theory of the specification of colors by means of the I. C. I. Standard Observer and Coordinate System,[2] and also the theory of visual range.[3] We shall commence by quoting the pertinent formulas from the latter theory.

## 2. ALTERATION OF CONTRAST BY THE ATMOSPHERE

It can be shown that any object of intrinsic luminance $B_0$, seen through a thickness $r$ of an atmosphere having an extinction coefficient $\sigma$, has the apparent luminance

$$B=B_0e^{-\sigma r}+B_h(1-e^{-\sigma r}). \tag{1}$$

Such an equation applies immediately to vision in the horizontal, when $B_h$ turns out to be the luminance of the horizon sky in the same azimuth as the object. For oblique vision, $\sigma=F(r)$, and, if we write,

$$\bar{R}=\int_0^R f(r)dr, \tag{2}$$

we may transform (1) into

$$B=B_0e^{-\sigma_0\bar{R}}+B_m(1-e^{-\sigma_0\bar{R}}), \tag{3}$$

where $\sigma_0$ is the value of the extinction coefficient at the lower end of the path, and where $B_m$ is an equilibrium luminance, frequently identical with the luminance of the horizon sky in either of two directions which depend on the position of the sun and the direction of the line of sight. In what follows we shall work under the assumption that Eq. (1) applies, always remembering the possibility of substituting $\sigma_0$, $B_m$, and $\bar{R}$ for $\sigma$, $B_h$, and $r$ respectively, and thereby dealing with oblique vision.

If Eq. (1) is true, it will certainly hold if we confine our attention to a narrow band of wave-lengths $d\lambda$, centered on the wave-length $\lambda$. This equation then becomes

$$B_\lambda=B_{0,\lambda}e^{-\sigma_\lambda r}+B_{h,\lambda}(1-e^{-\sigma_\lambda r}). \tag{4}$$

## 3. CHROMATICITY AND LUMINANCE OF A DISTANT OBJECT

In developing the consequences of this, we shall use as a unit of luminance that of the horizon sky, expressing all other luminances in terms of $B_h$. In the usual method[2] of weighted ordinates for calculating the chromaticity of an object under the illumination furnished by a source of spectral radiant emittance proportional to $W_\lambda$, we are furnished with a table of values of $W_\lambda\bar{y}_\lambda$, the entries in which add up to unity, or to 100 percent. If we use such a table, we may write

$$B_h=\int_0^\infty W_\lambda\bar{y}_\lambda d\lambda, \tag{5}$$

on the usual assumption that the horizon sky has the color of the prevailing illumination.‡ Then in Eq. (4)

$$B_{h,\lambda}=W_\lambda\bar{y}_\lambda. \tag{6}$$

Note that as $r$ increases without limit, $B_\lambda$ approaches $B_{h,\lambda}$ asymptotically. We now have to investigate $B_{0,\lambda}$.

Let us think first of an ideal white object seen against the horizon sky. Let its luminance as seen from a nearby point of observation ($r=0$) be $B_w$; its *contrast* with the horizon sky will be

$$C_w=(B_w-B_h)/B_h=(B_w/B_h)-1,$$

* Contribution from the Division of Physics, National Research Council of Canada, Ottawa. Issued as N. R. C. No. 2138.

† Presented at the New York Meeting of the Optical Society of America (March 1950).

[1] W. E. K. Middleton, Trans. Roy. Soc. Canada, Sec. III 29, 127 (1935). This paper was reprinted in a shortened form as an appendix to the book, *Visibility in Meteorology* (University of Toronto Press, Toronto, 1941), second edition.

[2] A. C. Hardy, *Handbook of Colorimetry* (Massachusetts Institute of Technology Press, Cambridge, Massachusetts, 1936).

[3] S. Q. Duntley, J. Opt. Soc. Am. 38, 179 (1948); J. Opt. Soc. Am. 38, 237 (1948).

‡ The earth not being flat, this condition is not quite reached when the air is very clear.

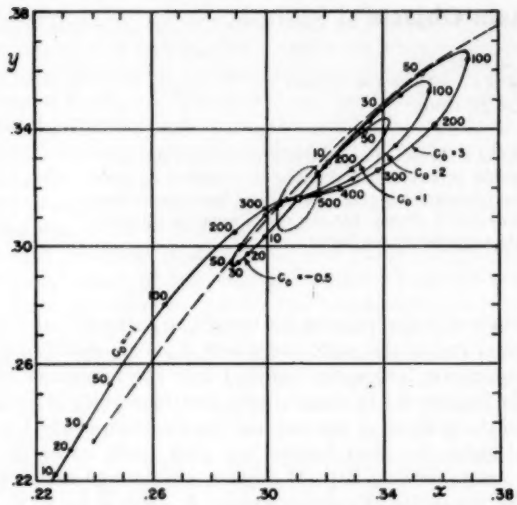


FIG. 1. Portion of the I.C.I. Mixture diagram showing the chromaticities of achromatic objects in pure air. The figures on the curves refer to distances in km. The broken line is the blackbody locus and the ellipse represents the locus of colors just discriminable from source "C."

and therefore

$$B_w=(C_w+1)B_h$$

and

$$B_{w,\lambda}=(C_w+1)B_{h,\lambda}. \tag{7}$$

Now let us replace the white object by another object geometrically similar, but this time of any color, defined by its spectral reflectance $f_\lambda$. Under these circumstances the apparent (monochromatic) luminance of the colored surface at $r=0$ is

$$B_{0,\lambda}=f_\lambda B_{w,\lambda}=f_\lambda(C_w+1)B_{h,\lambda}. \tag{8}$$

Substituting from (8) and (6) in (4), we obtain

$$\begin{aligned}B_\lambda&=[f_\lambda(C_w+1)e^{-\sigma\lambda r}+(1-e^{-\sigma\lambda r})]W_\lambda\bar{y}_\lambda\\&=[1+(f_\lambda C_w+f_\lambda-1)e^{-\sigma\lambda r}]W_\lambda\bar{y}_\lambda.\end{aligned} \tag{9}$$

In view of Eq. (5), the quantity in the square bracket in Eq. (9) can take the place of the reflectance in the ordinary expressions for the tristimulus values of a colored surface, and we can write down at once

$$\left.\begin{aligned}X&=\int_0^\infty W_\lambda\bar{x}_\lambda[1+(f_\lambda C_w+f_\lambda-1)e^{-\sigma\lambda r}]d\lambda\\Y&=\int_0^\infty W_\lambda\bar{y}_\lambda[1+(f_\lambda C_w+f_\lambda 1)-e^{-\sigma\lambda r}]d\lambda\\Z&=\int_0^\infty W_\lambda\bar{z}_\lambda[1+(f_\lambda C_w+f_\lambda-1)e^{-\sigma\lambda r}]d\lambda\end{aligned}\right\}, \tag{10}$$

the chromaticity coordinates being found as usual:

$$x=\frac{X}{X+Y+Z},\quad y=\frac{Y}{X+Y+Z},\quad z=\frac{Z}{X+Y+Z}. \tag{11}$$

Equations (10) are believed to be the most general possible expression of this theory, and should replace the corresponding formulas in the 1935 paper. If $f_\lambda=0$ for all values of $\lambda$ (black object), they reduce to

$$X=\int_0^\infty W_\lambda\bar{x}_\lambda(1-e^{-\sigma\lambda r})d\lambda,\quad \text{etc.}; \tag{12}$$

if $f_\lambda$ is a constant but different from zero (achromatic object) it is sometimes preferable to write them

$$X=\int_0^\infty W_\lambda\bar{x}_\lambda(1+C_0e^{-\sigma\lambda r})d\lambda,\quad \text{etc.}, \tag{13}$$

where $C_0$ is the contrast between the achromatic object and the sky at $r=0$.

In this analysis we have made $C_w$ and $C_0$ constant. This is a result of the hypothesis that the horizon sky is the color of the prevailing illumination. If this is not sufficiently exact, we may consider $W_\lambda$ as the spectral radiant emittance of the horizon sky, and allow $C_w$ (or $C_0$) to be a function of $\lambda$; but it is unlikely that in practice the data will have a precision which justifies such a refinement.

The application of Eq. (10), (12), or (13) requires the following data: (1) The energy distribution of the illumination from sun and sky. In the absence of actual measurements, it is convenient to assume a distribution similar to that of sunlight above the atmosphere,[4] or as an approximation to this, I. C. I. source "C." (2) The value of $\sigma$ at each value of $\lambda$ within the visible spectrum. For dense country fogs it is constant, or nearly so; the most marked variation would be in pure air, entirely free from particles larger than the molecules of the atmospheric gases. For such air, $\sigma=0.00106\lambda^{-4.08}$ km$^{-1}$ very nearly, at 1013.2 mb and 273°K. (3) The spectral reflectance $f_\lambda$ of the object. In the absence of this information, the "short method" given in the 1935 paper can be used, with better approximation the less selective the air and the darker the color of the object at $r=0$.

## 4. NUMERICAL EXAMPLES

To illustrate the application of this theory, we have calculated the apparent chromaticity of achromatic objects in pure dry air, and also of objects the color of a sample of growing grass, spectrophotometered in this laboratory, and the color of the paint known as International Orange, much used on various structures at airports. The illumination is supposed to be source "C." The results for the achromatic objects are shown in Fig. 1, for the others in Fig. 2. These diagrams are small portions of the chromaticity chart and a portion of the blackbody locus is shown for easier orientation.

In Fig. 1 there is a curve for each of six values of intrinsic contrast, $C_0$, from $-1$ (black object) to $+3$,

[4] Reference 2, p. 18.

which is probably nearly as high as can be found between the horizon sky and a snow field in full sunlight. The contrast of grey objects of luminance factor $\beta<0.25$ with the sky will probably never be positive. It was formerly thought that under an overcast sky $C_0=-1+\frac{1}{2}\beta$ for any achromatic object, but the writer showed[6] in 1947 that this is far from correct, and that in extreme cases $C_0$ can reach about $+0.8$ for a white object under such conditions. In general, however, the positive values will apply only to objects of high luminance factor on which the sun is shining.

In this figure is also shown an ellipse, which is plotted from the data of MacAdam.[6,7] This represents the locus of colors which are just distinguishable from source $C$, and is three times the size of the corresponding ellipse in reference 7, which results from the standard deviation of matches. The ratio three was suggested by MacAdam.[8]

It will be seen at once that all these colors lie fairly near the blackbody locus, those with $C_0>0$ being pale orange and those with $C_0<0$ pale blue. Naturally the curve for $C_0=0$ shrinks to a point at source "$C$", because this is the condition of "optical equilibrium," in which the luminance and color of objects are unchanged by distance. The curve for $C_0=-1$ (black object) is not closed, but all the others are, and in theory the curve for a very nearly black object will be closed, with one arm covering only a very small range of $r$. At a very short distance such objects appear an unsaturated blue, but the very low luminance might prevent the observation of this.

The fact that the colors lie along the blackbody locus also makes it certain that the same general results would be obtained for any actual energy distribution likely to be found in daylight, which would itself have a color near the locus. The calculations therefore demonstrate that while dark objects look blue in the distance—the more saturated, the clearer the air—distant snowfields, clouds and other objects of high positive contrast look pale orange. This color, usually referred to as yellow, was mentioned by de Saussure[9] and has been illustrated by Heim.[10]

The curve for the black object passes precisely through the point $x=0.240$, $y=0.245$ given by Hess and Linke[11] as the chromaticity of the bluest blue sky. It is really the "blue of the sky," of course, that lies in front of the distant hill. Further experimental confirmation comes from Hendley and Hecht,[12] who found by direct comparison with Munsell papers that distant objects approach the hue of 475 mμ, almost exactly that calculated for dark objects at about 20 km.

One interesting feature of the diagram is that the dominant wave-length is a function of $r$ but almost independent of $C_0$ at constant $r$, except that it passes to the complementary as $C_0$ changes sign.

Let us now consider the colored objects (Fig. 2). The green goes into the blue region before returning to the chromaticity of the illuminant, and approximate calculation shows that this behavior is shared by other colors of only moderate purity and value. The greatest purity in the blue is reached in a few tens of kilometers, but on the way to this the locus passes rather near the achromatic point, and at about 5 km the color would probably appear a very slightly greenish grey, having about 30 percent the luminance of the horizon.

As is shown better by the curves for International Orange, the intrinsic contrast determines to some extent how far toward the blue the apparent color goes. At high values of $C_w$ the apparent colors of grass and orange approach the achromatic point from hues roughly complementary, and the color contrast between them drops below threshold only at about the visual range. Presumably, therefore, the visibility of small areas of International Orange will be optimum against grass, and probably other green foliage. These orange colors are also in a region of the chromaticity diagram where, according to Middleton and Holmes,[13] not much change of hue results from decreased angular dimensions.

## 5. EXTENSION TO OTHER ATMOSPHERES

These calculations pertain to the most selective atmosphere possible. In a non-selective atmosphere,

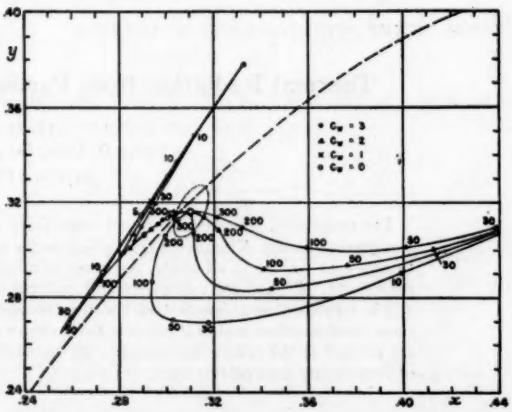


FIG. 2. Portion of the I.C.I. Mixture diagram showing the chromaticities in pure air of grass and of International Orange paint. The figures on the curves refer to distances in km. The broken line is the blackbody locus and the ellipse represents the locus of colors just discriminable from source "$C$."

[5] W. E. K. Middleton, Quart. J. Roy. Meteor. Soc. **73**, 456 (1947).
[6] D. L. MacAdam, J. Opt. Soc. Am. **32**, 247 (1942).
[7] D. L. MacAdam, J. Opt. Soc. Am. **33**, 18 (1943).
[8] Reference 6, p. 262.
[9] H. B. de Saussure, Mem. de l'Acad. de Turin **4**, 409 (1789).
[10] A. Heim, *Luft-Farben* (Hofer and Company, Zurich, 1912).
[11] P. Hess and F. Linke, Meteorol. Zeits. **59**, 313, 364, 368, 400 (1942).
[12] C. D. Hendley and S. Hecht, J. Opt. Soc. Am. **39**, 870 (1949).
[13] W. E. K. Middleton and Marian Holmes, J. Opt. Soc. Am. **39**, 582 (1949).

for example a dense fog, the locus of apparent colors is, of course, a straight line joining the chromaticity of the color at $r=0$ to the achromatic point. Without any calculation, the general trend of the locus in atmospheres of moderate selectivity will be obvious. Calculations, not reported here, have been made for a very light haze, with no unexpected results.

### 6. LIMITATIONS OF THE THEORY

As every colorist knows (but does not always emphasize), the I. C. I. coordinates do not *describe* colors, but only assign numbers to colors which designate their chromaticity and luminance. The theory takes no account of such attributes as gloss or texture, and does not differentiate between various modes of appearance. It is also important to recognize that the experiments on color mixing which are at the base of the I. C. I. color metric were made with aperture colors in a field 2° in angular diameter; and while it is known that the resulting data are valid for surface colors and for somewhat larger fields, very curious changes take place in color vision when we go to fields of a few minutes of angle or less, when the entire pattern of color perception alters.[13] These phenomena must be taken into account in any prediction of the appearance of a distant object of moderate dimensions. Nothing *quantitative* is known at the time of writing about the appearance of colors of small subtense against strongly chromatic backgrounds, but the experiments of H. Hartridge may serve as a guide.[14]

[14] H. Hartridge, Phil. Trans. Roy. Soc. London **B232**, 519 (1947).

### 7. THE VISUAL RANGE OF COLORED OBJECTS

It was originally believed that there should be a separate theory of the visual range of colored objects, taking into account the contrast in chromaticity between the object and its background as well as the contrast in brightness. If, however, we refer to the MacAdam ellipse in Fig. 2, we shall see that by the time the object has reached its visual range, its color is within the ellipse or very near it. Furthermore, the threshold of chromaticity difference will increase greatly below a subtense of about half a degree. Since few marks of any striking color are likely to be as large as this, we may conclude that for practical purposes no special theory of the visual range of colored objects is necessary, and that colored marks will behave in the same way at their visual range as grey ones of the same luminance factor.

By making calculations about an extreme case it is possible to show that in a fog, for example, a large brightly colored object might just remain visible by virtue of its chromaticity contrast alone. If, for instance, we suppose an International Orange surface in a shallow fog, and that $C_w=3$ (this may be too high for such conditions, but we are taking an extreme example), we find that the contrast falls to 0.02 at a distance $V=0.695V_2$, where $V_2$ is the meteorological range.[3] At this distance the chromaticity of the object turns out to be $x=0.322$, $y=0.321$, which is well outside the ellipse of Fig. 2; but even such an object would have to subtend a degree or so to lie outside the threshold for certain; and if we then removed it to $r=0.8V_2$, we should find its chromaticity on the ellipse.

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# Thermal Radiation from Partially Transparent Reflecting Bodies

H. O. McMAHON
*Arthur D. Little, Inc., Cambridge, Massachusetts*
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The emissivity, transmissivity, and reflectivity are considered in detail for heated, reflecting, partially transparent bodies. Kirchhoff's law, which in its usual form applies only to opaque bodies, is generalized to apply to matter of all kinds. An exact solution is found for the relationships between the "apparent reflectivity," $R^*$, and the true reflectivity and true transmissivity. Similarly, the "apparent transmissivity," $T^*$, is expressed as a function of the true transmissivity and true reflectivity. Further development of these considerations makes it possible to construct a ternary chart in which the observables $E$, $T^*$, and $R^*$ are plotted at the apices of a triangle, the true transmissivities and reflectivities then appear as a system of intersecting lines on the chart.

### INTRODUCTION

ALL matter radiates when heated, the resulting spectral intensity depending upon certain intrinsic characteristics of the material such as absorption coefficient and refractive index, and also upon some superficial characteristics such as geometry and surface roughness. The functional relationships among the experimentally measurable quantities, emissivity, apparent reflectivity, and apparent transmissivity have been expressed adequately only for the limiting conditions of an opaque material, that is, one for which the apparent transmissivity is zero. For this condition

Kirchhoff's law relates spectral emissivity to spectral reflectivity, which in its simplest form may be written

$$J(\lambda, t)=J_b(\lambda, t)\{1-R(\lambda, t)\}.$$

$J(\lambda, t)$ is the emissive power of the body at the temperature $t$ and in the wave-length region $\lambda$ to $(\lambda+d\lambda)$, that is, the time rate of radiant energy emitted throughout a solid angle of $2\pi$-steradians from a surface area of 1 cm$^2$; $R(\lambda, t)$ is the reflectivity of the body for the same temperature and wave-length, and $J_b(\lambda, t)$ is the spectral emissive power of an ideal blackbody. The ratio of $J(\lambda, t)$ to $J_b(\lambda, t)$ is the spectral emissivity;

$$E(\lambda, t)=J(\lambda, t)/J_b(\lambda, t).$$

Kirchhoff's law may then be written simply as

$$E(\lambda, t)=\{1-R(\lambda, t)\}.$$

For a body which is partially transparent either because of good transmission characteristics or small thickness, Kirchhoff's law cannot be applied directly. This is a consequence of the fact that the law derives from the necessary existence of an energy balance between emission and absorption for a body in temperature equilibrium with a uniformly heated enclosure. For an opaque body all the radiation impinging upon it must either be reflected or re-emitted; for a partially transparent body, on the other hand, a portion of the impinging radiation is transmitted and emerges, some portions only after one or more internal reflections. It is clear, therefore, that the transmissivity, $T(\lambda, t)$, must occur as a parameter in a more general expression than that of Kirchhoff which will apply to all bodies in general and to opaque bodies as a limiting case when $T(\lambda, t)=0$.

## THE EMISSIVITY

Within the transparent body radiation is being generated and absorbed simultaneously. Radiation generated within a given region must journey to the surface before being emitted. While passing through the material it is attenuated in accordance with Lambert's law, and again at the surface a fraction of it is reflected back into the interior. Of the fraction reflected back many traversals and many reflections must occur before the radiation originally generated has become completely attenuated through the combined effects of escape through the surface and absorption in the material.

In a transparent slab having plane parallel faces as indicated in Fig. 1, the radiation generated in a 1-cm$^2$ layer of material $dx$ cm thick is $j(\lambda, t)dx$, where $j(\lambda, t)$ is the volume spectral emissive power, that is, the time rate of radiant energy production within a 1-cm cube in the wave-length region $\lambda$ to $\lambda+d\lambda$. For unit solid angle the emitted intensity is $(1/4\pi)j(\lambda, t)dx$, and for a very small solid angle $d\omega$, containing radiation traveling essentially normal to the surface of the slab, the intensity is $(1/4\pi)j(\lambda, t)dxd\omega$. If the imaginary layer

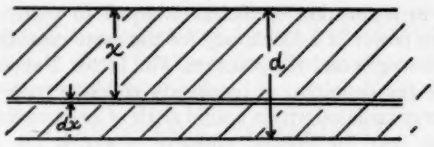


FIG. 1. A slab of partially transparent medium with reflecting surfaces.

lies at a depth of $x$ cm below the surface of the body, only a fraction equal to $e^{-k(\lambda, t)x}$ of the normal radiation will arrive at the surface; where $k(\lambda, t)$ is the absorption coefficient characteristic of the particular wave-length and temperature. The intensity arriving at the surface from this layer is then

$$(1/4\pi)j(\lambda, t)e^{-k(\lambda, t)x}dxd\omega.$$

The total normal radiation arriving at the surface, excluding residues from primary and higher order reflections, will be the summation of the above expression for all layers between $x=0$ and $x=d$, the thickness of the slab. The total normal radiation arriving as a result of emission is, therefore,

$$\frac{1}{4\pi}j(\lambda, t)d\omega\int_0^d e^{-k(\lambda, t)x}dx,$$

which becomes on integration

$$\frac{j(\lambda, t)}{4\pi k(\lambda, t)}[1-e^{-k(\lambda, t)d}]d\omega.$$

Since $\exp[-k(\lambda, t)d]$ is by definition the true transmissivity of the slab, this term can be substituted by $T(\lambda, t)$. The expression for the integrated result then becomes

$$\frac{j(\lambda, t)}{4\pi k(\lambda, t)}\{1-T(\lambda, t)\}d\omega.$$

If the reflectivity is $R(\lambda, t)$, the radiation which penetrates the surface and escapes is:

$$\{1-R(\lambda, t)\}\frac{j(\lambda, t)}{4\pi k(\lambda, t)}\{1-T(\lambda, t)\}d\omega.$$

If the body is opaque either because of a large value of $k(\lambda, t)$ or $d$, Kirchhoff's law may be applied. For this condition $T(\lambda, t)$ becomes zero and we may write:

$$\{1-R(\lambda, t)\}\frac{j(\lambda, t)}{4\pi k(\lambda, t)}d\omega=\frac{J_b(\lambda, t)}{2\pi}\{1-R(\lambda, t)\}d\omega.$$

From this we conclude

$$\frac{j(\lambda, t)}{k(\lambda, t)}=2J_b(\lambda, t) \quad \{\text{for } T(\lambda, t)=0\}.$$

The expression shows that the ratio of volume emissive

power to absorption coefficient is equal to twice the emissive power of a blackbody for the same conditions of wave-length and temperature. The factor 2 appears because the definition of blackbody emissive power is the energy radiated within a solid angle of $2\pi$-steradians, whereas that for volume emissive power is for $4\pi$-steradians.

Returning to the expression for the sum of the non-reflected portion of radiation which arrives from the lower regions and penetrates the surface of a transparent slab, we may write this as:

$$\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

The portion reflected passes through a layer of material of thickness $d$, is again reflected from the rear surface, is then transmitted through another $d$ cm, and a portion of this emerges as a second contribution. The emerging portion will have an intensity of

$$R^2(\lambda, t)\cdot T^2(\lambda, t)\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

This process of reflection will occur again with the result that the third contribution will have an intensity of

$$R^4(\lambda, t)\cdot T^4(\lambda, t)\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

The total emerging radiation is the sum of all even terms to infinity.

$$\sum_{\substack{n=0\\ \text{even}\\ \text{only}}}^{n=\infty} R^n(\lambda, t)\cdot T^n(\lambda, t)\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

So far, only that radiation emitted toward the front surface has been considered. Radiation emitted toward the rear surface is partially reflected and a fraction of this escapes through the front surface. Again it can be shown that the sum of all components of radiation initially directed toward the rear surface but finally emerging from the front surface is given by an infinite series

$$\sum_{\substack{n=1\\ \text{odd}\\ \text{only}}}^{n=\infty} R^n(\lambda, t)\cdot T^n(\lambda, t)\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

The total emission from the front face is then the sum of the two series of odd and even values of $n$. This sum is of course equal to the spectral emissive power of the body multiplied by the solid angle $d\omega$.

$$J(\lambda, t)\frac{d\omega}{2\pi}=\sum_{\substack{n=0\\ \text{all values of } n}}^{n=\infty} R^n(\lambda, t)\cdot T^n(\lambda, t)\times\{1-R(\lambda, t)\}\frac{J_b(\lambda, t)}{2\pi}\{1-T(\lambda, t)\}d\omega.$$

Since $R(\lambda, t)$ and $T(\lambda, t)$ are both always less than unity, the infinite series may be written in analytical form giving the result

$$J(\lambda, t)=\frac{\{1-R(\lambda, t)\}\{1-T(\lambda, t)\}J_b(\lambda, t)}{\{1-R(\lambda, t)\cdot T(\lambda, t)\}}.$$

The emissivity, by definition, is the ratio of actual emitted energy to that of a blackbody,

$$E(\lambda, t)=\frac{J(\lambda, t)}{J_b(\lambda, t)}.$$

Therefore,

$$E(\lambda, t)=\frac{\{1-R(\lambda, t)\}\{1-T(\lambda, t)\}}{\{1-R(\lambda, t)\cdot T(\lambda, t)\}}.$$

It is to be noted that when $T(\lambda, t)$ is zero, which is the case for opaque bodies, the emissivity is given by

$$E(\lambda, t)=1-R(\lambda, t)\quad[\text{when } T(\lambda, t)=0].$$

This is Kirchhoff's law in its usual form. On the other hand, we see that when $R(\lambda, t)$ is zero, as is the case for non-reflecting glasses or for luminous gas bodies to a first approximation, then

$$E(\lambda, t)=1-T(\lambda, t)\quad(R(\lambda, t)=0).$$

This is in agreement with the conclusions of Finkelnburg[1] relative to blackbody radiation from large gaseous bodies.

## THE APPARENT REFLECTIVITY

The normal reflectivity of a single surface of the transparent slab is $R(\lambda, t)$, but the apparent reflectivity $R^*(\lambda, t)$ is always greater than this because of multiple internal reflections which augment the primary reflection.

If the intensity of the incident normal radiation is $I_\lambda$, the intensity of the primary reflection is

$$I_\lambda R(\lambda, t).$$

A fraction $\{1-R(\lambda, t)\}$ penetrates the surface, and is reduced to the fraction $\{1-R(\lambda, t)\}T(\lambda, t)$ after traversing the body. This residue is partially reflected back with a fractional (relative to the original) intensity of $\{1-R(\lambda, t)\}T(\lambda, t)R(\lambda, t)$ and arrives at the underside of the front surface, diminished by a factor of $\{1-R(\lambda, t)\}T^2(\lambda, t)R^2(\lambda, t)$ of the original intensity $I_\lambda$. The penetrating intensity which will augment the primary reflection is then $I_\lambda\{1-R(\lambda, t)\}^2R(\lambda, t)T^2(\lambda, t)$.

Again, a portion is reflected into the body and this gives rise to an infinite series of contributions. The sum

[1] W. Finkelnburg, J. Opt. Soc. Am. 39, 185 (1949).

of all these makes up the total reflected intensity

$$I_\lambda R^*(\lambda, t) =$$

$$I_\lambda R(\lambda, t) + \sum_{n=1}^{n=\infty} \frac{I_\lambda\{1-R(\lambda, t)\}^2}{R(\lambda, t)}\{R^2(\lambda, t)\cdot T^2(\lambda, t)\}^n.$$

The exact value of this sum is

$$I_\lambda R(\lambda, t)+\frac{I_\lambda\{1-R(\lambda, t)\}^2 R(\lambda, t)T^2(\lambda, t)}{1-R^2(\lambda, t)\cdot T^2(\lambda, t)}.$$

The apparent reflectivity $R^*(\lambda, t)$ is obtained by dividing this quantity by $I_\lambda$, giving

$$R^*(\lambda, t)=R(\lambda, t)\left\{1+\frac{T^2(\lambda, t)\{1-R(\lambda, t)\}^2}{1-R^2(\lambda, t)\cdot T^2(\lambda, t)}\right\}.$$

It is to be noted that for a perfectly transparent body, that is, when $T(\lambda, t)=1$,

$$R^*(\lambda, t)=\frac{2R(\lambda, t)}{1+R(\lambda, t)} \qquad T(\lambda, t)=1$$

showing that the apparent reflectivity is approximately twice the true reflectivity for small values of $R(\lambda, t)$. It is only when $T(\lambda, t)=0$ that the apparent and true reflectivities are identical.

### THE APPARENT TRANSMISSIVITY

For the transparent slab with reflecting surfaces the apparent transmissivity will be less than the true transmissivity because of reflection losses. If the intensity of the incident radiation is $I_\lambda$, the fraction which penetrates into the interior is $\{1-R(\lambda, t)\}$ and the fraction which emerges from the opposite side is $\{1-R(\lambda, t)\}^2T(\lambda, t)$. Again, there will be contributions from multiply reflected residues, the total of which can readily be shown to be

$$I_\lambda\{1-R(\lambda, t)\}^2T(\lambda, t)\sum_{n=0}^{n=\infty} R^{2n}(\lambda, t)T^{2n}(\lambda, t).$$

Again, since $R(\lambda, t)$ and $T(\lambda, t)$ are always less than unity, the sum is expressed rigorously as

$$\frac{I_\lambda\{1-R(\lambda, t)\}^2T(\lambda, t)}{\{1-R^2(\lambda, t)\cdot T^2(\lambda, t)\}}.$$

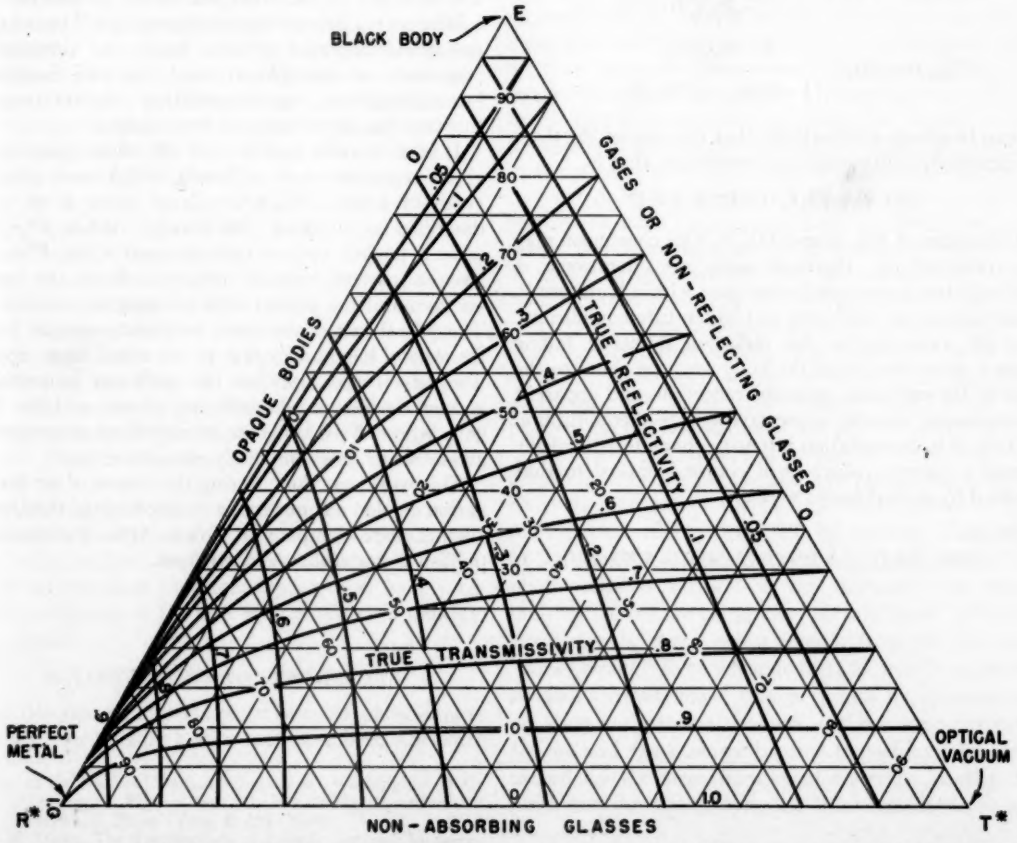


FIG. 2. Thermal radiation chart. $E$, $T^*$, and $R^*$ are emissivity, apparent transmissivity, and apparent reflectivity, respectively.

This is then the apparent transmitted intensity, $I_\lambda T^*(\lambda, t)$. So that

$$T^*(\lambda, t) = T(\lambda, t)\frac{\{1-R(\lambda, t)\}^2}{\{1-R^2(\lambda, t)\cdot T^2(\lambda, t)\}}.$$

A simple transmission experiment which actually measures $T^*$ will thus be in error if the result is interpreted simply as $T$, as is so often done in the usual absorption spectra measurements. However, the reflectivity of transparent substances is usually fairly low except in regions of very high absorption so that in most cases the resulting error may be small.

## THE THERMAL RADIATION CHART

The three directly measurable quantities emissivity, apparent reflectivity, and apparent transmissivity are interrelated by the three equations.

$$E(\lambda, t) = \frac{\{1-R(\lambda, t)\}\{1-T(\lambda, t)\}}{\{1-R(\lambda, t)\cdot T(\lambda, t)\}}$$

$$R^*(\lambda, t) = R(\lambda, t)\left\{1+\frac{T^2(\lambda, t)\{1-R(\lambda, t)\}^2}{1-R^2(\lambda, t)\cdot T^2(\lambda, t)}\right\}$$

$$T^*(\lambda, t) = T(\lambda, t)\frac{\{1-R(\lambda, t)\}^2}{\{1-R^2(\lambda, t)\cdot T^2(\lambda, t)\}}.$$

It can be shown algebraically that the sum of the three is identically unity under all conditions, that is,

$$E(\lambda, t)+T^*(\lambda, t)+R^*(\lambda, t)=1$$

for all values of $R(\lambda, t)$ and $T(\lambda, t)$. This conclusion may be confirmed by thermodynamic considerations. A partially transparent slab contained within a uniformly heated enclosure will come to temperature equilibrium. For all wave-lengths the radiation intensity falling upon a given portion of the body must be equal to the sum of the emission, apparent reflection, and apparent transmission, in order to preserve a state of equilibrium. If $J_b(\lambda, t)$ is the radiation intensity characteristic of the heated enclosure, which is of course identical to that emitted by a blackbody, we have

$$J_b(\lambda, t) = E(\lambda, t)J_b(\lambda, t)+R^*(\lambda, t)J_b(\lambda, t)+T^*(\lambda, t)J_b(\lambda, t)$$

from which

$$E(\lambda, t)+R^*(\lambda, t)+T^*(\lambda, t)=1.$$

This may be considered to be an expression of Kirchhoff's law in which it is extended to the partially transparent body.

It has been demonstrated that the sum of the observable quantities $E(\lambda, t)$, $R^*(\lambda, t)$, and $T^*(\lambda, t)$ is unity in all cases. This circumstance allows the construction of a triangular coordinate chart with $E(\lambda, t)=1$, $R^*(\lambda, t)=1$, and $T^*(\lambda, t)=1$ at the three apices, as shown in Fig. 2. On this chart there will be lines of constant $R$ (true reflectivity) and other lines of constant $T$ (true transmissivity) which represent the solution of the three equations of $E$, $R^*$, and $T^*$ in terms of $R$ and $T$. The complete thermal radiation properties of a given body at a particular wave-length and for a particular temperature are represented by a single point on the chart. The location of the point is determined experimentally by any two of the three observables $E$, $R^*$, and $T^*$. From the location of the point it is then possible to deduce exact values for $R$ and $T$. For any given temperature, as wave-length is varied, the reflectivity and transmissivity of the body will vary and the result will be a line on the triangular chart. In general there will be such a line for every temperature. The complete radiation properties of any body can therefore be described, in principle at least, by two families of intersecting lines, one representing constant temperature and the other constant wave-length.

It is of interest to note that the three apices of the chart represent three different well-known idealized types of bodies. When $E=1$ the body is of course described as an ideal "blackbody." When $T^*=1$ we have a perfect optical vacuum, and when $R^*=1$ we have a perfect metallic reflector. Both the optical vacuum and the perfect reflector have zero emissivity. The $T^*=0$ axis of the chart represents opaque bodies, for which Kirchhoff's law in its usual form applies. The $R^*=0$ axis describes the radiation properties of gaseous bodies or non-reflecting glasses and the third axis, where $E=0$ can best be described as crystals or glasses which are completely non-absorbing.

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# Application of Photoelectric Multiplier Tubes to the Sensitive Measurement of Absorption or of Changes of Relative Light Intensities

O. OLDENBERG AND H. P. BROIDA*
*Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts*
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The possibility of using photo-multipliers for the detection of the change in light intensity due to the absorption of free radicals in chemical reactions has been investigated. A discussion of the sensitivity of photo-tubes considers the effects of the random fluctuations of the photoelectric current, and the limitations due to the dark current and the fatigue of the tube. A balanced direct current circuit using two photo-multipliers is described. With this circuit, it is possible to detect a change of light intensity of 1 part in 10,000.

## I. INTRODUCTION

FOR a number of years experiments have been carried through at the physics laboratories of Harvard University for the purpose of applying the absorption spectra of free radicals to chemical analysis of gaseous reactions.[1] In this work many technical difficulties have arisen. One of the most serious handicaps is caused by the extremely small concentrations of free radicals in most chemical reactions, leading to very small amounts of absorption. Since the photographic plate at best can detect an absorption of the order of one percent, it has been necessary to provide very long path lengths to obtain sufficient optical depth for absorption experiments. With the development of sensitive photoelectric multiplier tubes, the detection of smaller amounts of absorption is made feasible.

Although photo-tubes have found many commercial and laboratory applications for the measurement of absorption in solids, liquids, and gases, possible extensions to sensitivity greater than about 1 percent have not been carefully investigated.

Our problem is essentially the same as the measurement of a small change of an intensity ratio treated by Dieke.[2] The most sensitive measurement of absorption will imply the most sensitive test for a change in relative intensities of two lines. As an outstanding difficulty Dieke mentions the fact that the balance of his bridge is not maintained if the total incident light intensity is changed. How to overcome this difficulty is our main problem.

We adapted the method to ultraviolet light in order to find weak absorption of the hydroxyl band at 3064A. Since in this region it is difficult to obtain a strong light source, the ten-stage photo-multiplier tubes were used to take advantage of the ease with which they amplify weak signals.

## II. LIMITATIONS TO SENSITIVITY

The description and characteristics of photo-multipliers are now reliably known and have been discussed fully by numerous investigators.[2,3] In the use of these tubes for sensitive measurements, it is important to know the limiting factors to the sensitivity of the tube and to distinguish clearly between the separate phenomena which may affect the photo-current. Our purpose is the detection of a small concentration of absorbing molecules, hence of a small absorption coefficient $\alpha$. This quantity is related to the change $\Delta I$ of the incident intensity $I$ by the relation $\Delta I/I=\alpha d$ ($d$=length of absorbing layer). Hence the measurement of a small absorption coefficient $\alpha$ is identical with the measurement of a small change of *relative intensity* of light. Because of the linearity of the photo-tubes, this relative change in light intensity will be equal to the relative change in the output current from the photo-tube. The smallest relative absorption which is detectable is limited by the fluctuations in the light source, in the photo-tube, and in the apparatus for observing the current from the anode of the tube. Each source of fluctuation must be eliminated or its effects compensated. The fluctuations in the light source intensity are of such a nature that they can be compensated for by a bridge arrangement to be described later. There are numerous arrangements of stable electrical systems for detecting the output current; the simplest of these is a sensitive direct current galvanometer. Under ideal conditions, the smallest detectable absorption is dependent on the fluctuation of the photo-current itself.

There are three independent factors which limit the applications of the photo-tube. (1) The ultimate sensitivity is inherent in the discontinuous nature of the photoelectric effect; there will be *random fluctuations* in the number of electrons per unit time leaving the photo-emissive surface of the cathode. The other limiting factors are caused by the tube itself. (2) With small signals, there is interference from the so-called *"dark-current."* Even when no light falls on the cathode, a small current flows; this is caused by spontaneous emission and external leakage. (3) For large currents, *fatigue* and *space charge* become important; these are caused by the large number of electrons leaving the ninth and the eighth dynodes. It is necessary to isolate

* Now at the National Bureau of Standards, Washington, D. C.
[1] O. Oldenberg, J. Phys. Chem. **41**, 293 (1937); O. Oldenberg and F. F. Rieke, J. Phys. Chem. **6**, 439 (1938).
[2] G. H. Dieke, The Transactions of Instruments and Measurements Conference, Stockholm (1937), p. 17.
[3] R. W. Engstrom, J. Opt. Soc. Am. **37**, 420 (1947).

and determine the effect of each of these disturbing factors.

### (1) Random Fluctuations

The fluctuation due to the randomness of the emission process is the ultimate physical limit on the sensitivity of the photo-tubes. The current from the cathode $i_c$ is given by

$$i_c = ne, \tag{1}$$

where $n$ is the number of electrons emitted per second and $e$ is the charge on the electron. There is an amplification of this current at each dynode of the multiplier tube such that an over-all amplification $\mu$ is obtained. The output current $i$ is

$$i = \mu i_c = \mu ne. \tag{2}$$

There will be a fluctuation $\Delta i$ of the output current which depends upon the fluctuation of the photo-current from the first surface. The relative fluctuation of the output current is equal to the relative root mean square fluctuation at the cathode. If $t$ is the time constant of the galvanometer (the equivalent band width in an a.c. measuring technique is one-fourth the reciprocal of $t$), the average relative root mean square fluctuation of the cathode current is the reciprocal of $(nt)^{\frac{1}{2}}$, and therefore the relative output fluctuation is

$$\Delta i/i = 1/(nt)^{\frac{1}{2}}. \tag{3}$$

The average number of electrons per second leaving the cathode can be expressed in terms of the measured output current by making use of Eq. (2).

$$\Delta i/i = (\mu e/it)^{\frac{1}{2}}. \tag{4}$$

There is also a small fluctuation of less than 15 percent of the relative fluctuation due to the randomness of the process of secondary emission from the dynodes. This superimposed effect will not be further considered because it is relatively unimportant.

It is important to notice that with increased amplification $\mu$ and the same output current, the relative fluctuations are increased (Eq. (4)). This amounts to a decrease in the sensitivity of the detector. As the amplification $\mu$ is increased and the output current kept constant, the number of photo-electrons leaving the cathode is decreased and the average relative fluctuation is increased. Thus in any measurement for which the highest sensitivity is required, it is requisite that the light intensity be as large as possible so that the amplification can be decreased. It is useful to estimate the smallest relative change in light intensity that can be detected with present photo-tubes. This is done by assuming sufficient light intensity for the maximum output current of $10^{-4}$ ampere, a galvanometer time constant of one second and, furthermore, supposing that the smallest absorption that can be detected is given by the fluctuation stated in Eq. (4); that is, that the smallest relative change $\Delta i/i$ that can be detected is given by

$$\left(\frac{\Delta i}{i}\right)_{\min} = \left(\frac{\mu e}{it}\right)^{\frac{1}{2}} = \left[\frac{\mu(1.6)10^{-19}}{(10^{-4})1}\right]^{\frac{1}{2}} = 4\times10^{-8}(\mu)^{\frac{1}{2}}.$$

For a single stage tube, $\mu$ is equal to one, and

$$(\Delta i/i)_{\min} = 4\times10^{-8}.$$

It is not uncommon to have an amplification factor of over a million in the more sensitive photo-multiplier tubes; this leads to

$$(\Delta i/i)_{\min} = 4\times10^{-5}.$$

This computation, which is based on the actual data, shows that the multiplication by secondary electron emission is undesirable if we are able to produce the same maximum output by sufficiently intense light at the photoelectric surface. Since in many experiments this is impossible, practically the multiplication provides a great improvement. With existing tubes, the only manner in which this relative mean fluctuation can be further decreased is by increasing the time of observation. Since this will affect the sensitivity only inversely as the square root, these minima can be changed but slightly. Under any practical conditions, there are frequently many other factors which make it difficult and frequently impossible to reach this ultimate sensitivity.

### (2) Dark Current

The dark current sets a lower limit to the signal which can be observed. Although the dark current is an important and often disturbing effect, generally it can be eliminated as a disturbance by special precautions. Most multiplier tubes have a dark current of the order of $10^{-8}$ ampere, and an exceptionally good tube may have a dark current as low as $5\times10^{-11}$ ampere. At times it appears that a tube has a dark current greater than $10^{-8}$ ampere; in almost every case this is due to faulty external wiring causing leakage, or lack of precautions for keeping moisture from the tube surface. It is possible to balance out the steady component of the dark current so that it will have no effect on measured currents; and when necessary, cooling to liquid air temperatures reduces the dark current by a factor of one hundred if it is due to thermal emission.[4] Regenerative ionization, which is associated with complete breakdown and uncontrollable discharge, is another type of dark current; this occurs only if the voltage per stage is greater than that specified by the manufacturer.

### (3) Fatigue

From Eq. (4) it is seen that the relative fluctuations will be decreased by an increase in the output current.

[4] B. H. Rank and R. V. Weigand, J. Opt. Soc. Am. 36, 325 (1946).

However there is a maximum current that can be obtained, since at approximately a milliampere the current is limited by a space charge. Strangely enough, because of the geometrical construction, this space charge occurs in the multiplier tubes at the surface of the eighth dynode rather than at the ninth dynode as might be expected. However, in most practical equipment, the limitation of the method occurs at smaller currents than that at which the space charge becomes noticeable; this limitation is known as fatigue. Fatigue is the phenomenon characterized by a loss of sensitivity of the tube with continued use. There is also the allied characteristic of a slow return to the initial sensitivity if the tube is left in darkness. Since the current is largest at the ninth dynode, fatigue occurs mainly on this surface. Fatigue is quite apparent for output currents of a tenth of a milliampere, and for many purposes it is negligibly small at a microampere. Nevertheless even at this latter current, rapid changes of light intensity can cause fatigue which we can not neglect since we are interested in the measurement of the smallest relative changes.

Therefore there is an upper and a lower limit to the output currents of photo-tubes. On the high current side are the fatigue and space charge effects and on the low current side is the dark current.

### III. BALANCED PHOTO-TUBE CIRCUIT

For laboratory work, it is desirable to have a sensitive detector which can operate over a wide range of light intensity. A relatively inexpensive, easy-to-construct, direct current apparatus has been found to be advantageous. Since most articles in the literature emphasize alternating current or pulse methods for use with photo-multiplier tubes, it is worthwhile to point out the simplicity of a direct current circuit which sacrifices none of the sensitivity or ease of use of the other methods.

Figure 1 shows the schematic arrangement of the electrical connections to a single multiplier tube. For any application in which the highest sensitivity is required, the voltage probably is best supplied by dry batteries.[5] Power packs supplied by a.c. mains too often have small fluctuations which will show up when working with very small currents. It appears that for most purposes the use of batteries is less troublesome;

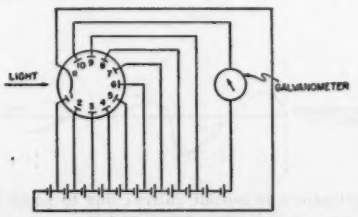


FIG. 1. Fundamental circuit for single photo-multiplier tube.

[5] R. B. Janes and A. M. Glover, R.C.A. Rev. 6, 43 (1941).

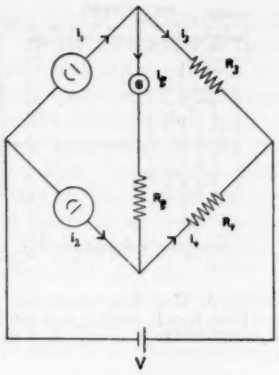

FIG. 2. Bridge circuit for comparing two light intensities.

and since the current furnished by them is very low, being of the order of microamperes, the batteries should last their shelf life. Moreover with such low current requirements, small-sized batteries can be used. By using an arrangement of taps on the batteries, the amplification can be varied over a wide range to compensate for various light intensities. It is much easier to reduce the output current by varying the voltage on the photo-tube than to adjust the optical intensity.

Since it is impossible to operate a light source with absolutely constant intensity, in absorption work it is necessary to split the light coming from the source into two paths, one through the absorber, the other, acting as a monitor, outside the absorber. These two beams act on separate photo-tubes. The difference of the photo-currents indicates the loss of light by absorption. For very sensitive measurements, both photo-tubes must see exactly the same source so that any changes within the source affect both equally. It is also important that no changes of temperature or pressure be able to displace one of the light paths. Such a displacement can move the light beam partly from the photo-cathode. The cathode surface itself is irregular in its sensitivity and it is important to keep the light beam rigid. A large diffuse light which covers the whole cathode provides the best source.

A bridge circuit such as the one in Fig. 2 will measure directly the difference between the light intensities on the two tubes. By applying Kirchhoff's circuit laws to the bridge, we express the galvanometer current $i_g$ in terms of the photoelectric currents $i_1$ and $i_2$ and the resistances $R_3$, $R_4$, and $R_g$ as follows:

$$i_g=\frac{R_3 i_1-R_4 i_2}{R_3+R_4+R_g}.$$

Where there is no absorbing medium in either path, we adjust the resistances so that $i_g=0$. This adjustment is independent of fluctuations in the light source since $i_1/i_2$ is constant over a wide range of light intensities. Now a deflection of the galvanometer is sure to indicate

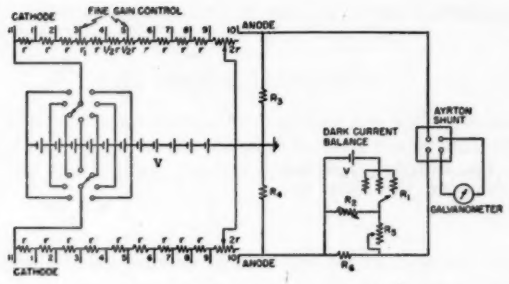


FIG. 3. Complete circuit for photo-multipliers. $r=2\times10^6\Omega$; $r_1=10^6\Omega$; $R_3=R_4=10^6\Omega$; $R_1=10^3$, $10^4$, $10^5\Omega$; $R_2=10$–$100\Omega$ decade; $R_5=100$–$1000\Omega$ slide wire; $R_6=10\Omega$; $V=1000$ volts; $v=2$ volts.

absorption of light. If $i_1$ measures the light intensity passing through the absorber, it will decrease by an amount $\delta i_1$ as the absorption in the test medium increases. Assuming $i_2$ to remain constant (except for changes due to fluctuations in the source which are compensated by corresponding changes $i_1$), and calling the current through the galvanometer due to the absorption of light $I_g$, it is seen that

$$I_g=\frac{\delta i_1}{1+(R_4/R_3)+(R_g/R_3)}. \qquad (6)$$

For symmetry reasons, $R_4$ is taken equal to $R_3$; and in usual practice $R_g$ can be made small compared to $R_3$. In this case, the current through the galvanometer is just one-half the change in current due to the absorption.

Curiously, Eq. (6) shows that the non-symmetrical bridge can be made twice as sensitive as the symmetrical bridge. If $R_g$ and $R_4$ are taken as very small compared to $R_3$, then the galvanometer measures directly the change in current.

Figure 3 shows the complete circuit for a balance photo-tube arrangement which has been found to be convenient and versatile; this is still the bridge circuit of Fig. 2. With this circuit it is possible to measure with relative ease, absorption from 0.01 to 100 percent for light sources whose mean intensity is reasonably constant. The use of a voltage divider introduces no observable fluctuations in the voltages and has the advantage of requiring fewer leads than direct connections to the battery terminals. The taps on the batteries providing rough gain controls make this set-up variable over a range of intensities greater than one hundred and allow the bridge to be balanced over this wide range without the need to disturb the optical path. With the fine gain control on the third and fifth dynodes of one tube, it is easily possible to balance the bridge to great precision.

The operator must keep in mind that a large deflection of the galvanometer should be produced rather by a high intensity of the source of light than by a large multiplication factor $\mu$.

The dark current of a properly connected and protected photo-multiplier is steady within 1/100 of its full value. The obvious procedure would be to equalize the dark currents of the two photo-multipliers by giving one of them a high parallel resistance. However this is impractical since the accurate adjustment of the high resistances needed is awkward. The arrangement shown in Fig. 3 is easier to operate. Here the galvanometer current (which in darkness, assuming the simpler circuit of Fig. 2, would show the difference of the dark currents) is reduced to zero by a counter electromotive force which is due to a weak adjustable current supplied through the resistance $R_5$. This particular suggested set of resistances allows a variation of dark current differences to be balanced out over a range from $4.5\times10^{-8}$ to $0.98\times10^{-11}$ ampere.

The inability to reach any greater sensitivity with the balanced arrangement of two tubes is connected with the fatigue effects.[6] This was determined by observing how large changes of intensity affected the zero balance of the two tubes. Reasons for the difficulty in keeping the bridge balanced have not been generally recognized. The unbalance comes from the differences in fatigue and recovery of the two tubes. Although fatigue effects are generally negligible for currents of the order of a microampere, for measurements to one part in ten thousand or better, even small fatigue is important. This unbalancing due to the fatigue is best understood by reference to Fig. 4; the figure is only intended to be diagrammatic and does not represent qualitative measurements. The gradual change of photo-current is caused by the tube itself, and the big step is caused by a change of light intensity. This figure shows the possibility of fluctuations in the galvanometer current which are due to fatigue even though the fatigue and the changes of light intensity are small.

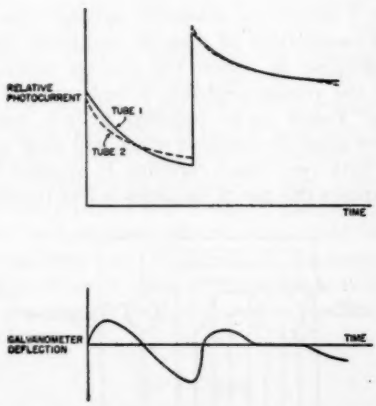


FIG. 4. Fluctuations in output current due to small differences in fatigue characteristics.

[6] K. G. Kessler and R. A. Wolfe, J. Opt. Soc. Am. **37**, 133 (1947).

It would be possible to overcome the fatigue problems associated with the use of two tubes by using a single tube on which light could be made to fall alternately from the test beam and from the monitor beam. The a.c. signal could be detected by the usual electronic techniques. Of course the electronic circuits would have to be designed for the sensitivity desired; and except for construction problems this should offer no difficulties since the photo-multipliers are a high impedance source. However, no matter what particular electrical system is used, for precision work it is necessary that the photo-tube should see the same source from the same direction in both the test and monitor beams.

When great care has been taken in the electrical connections so that there is no external leakage, it has been found possible to measure a relative change of light intensity of one part in ten thousand. This was done with several different sources; the only requirements are that the random fluctuations are less than this relative change and that the output current is less than that causing excessive fatigue (about a microampere). We also found it advantageous to select two tubes of nearly equal dark currents and sensitivity. The General Electric Company kindly supplied a pair of matched photo-multipliers, GL-931-A. For the measurements of the small currents associated with photo-tubes, it is necessary to take the usual precautions to avoid leakage. One of the largest leakage sources occurs in the tube socket; the newer tubes come with non-hygroscopic bases. It was found advantageous to use clip leads to the photo-tube and to support the tube with a Bakelite holder around the base. All difficulties with leakage during humid weather were avoided by soaking the base for thirty minutes in ceresin wax heated to a point just above the melting point. A stream from a high pressure nitrogen tank was used to blow off the excess wax, leaving only a thin protective cover. Cooling of the photo-multiplier for the suppression of the dark thermionic emission will be necessary only if the source of light is unusually weak.

It is often desirable to be able to check the linearity, sensitivity, fatigue, and dark current characteristics of the photo-tubes. Some of this can be done with little additional equipment. A switch is easily put into the circuit of Fig. 3 so that the output current from either tube can be read directly on the galvanometer. A set of calibrated screens and filters designed to fit into the light path near the source makes it possible to check the linearity, fatigue, and spectral response. Some sort of standard lamp can be used for determining the relative sensitivity of various tubes and for observing the change of sensitivity with continued use.

The main result is as follows. Our aim is the most sensitive measurement of *intensity differences*, which is needed for the detection of weak absorption and small changes of relative intensities. It is important that such disturbances as *leakage* and *fatigue*, which for ordinary measurements may be negligible, be carefully compensated. Leakage is largely removed by special treatment of the tubes; any residual leakage is compensated by the circuit of Fig. 3. Fatigue is compensated by selecting a pair of tubes of equal fatigue or, presumably still better, by having the two beams of light acting alternately on the same tube.

In our attempt to find weak absorption due to hydroxyl, we were able to measure an absorption of one-tenth of one percent to an accuracy better than ten percent. The light source of the hydroxyl emission was a discharge through water vapor using 60 cycle a.c. currents of the order of 100 milliamperes. A medium size quartz Hilger Spectrograph was the dispersing instrument. A slit placed in the focal plane of the spectrograph selected light at 3090A from the superimposed intense rotational lines $Q_1(7\frac{1}{2})$, $Q_2(1\frac{1}{2})$, and $Q_2(2\frac{1}{2})$ of the O→O band. Due to continuous absorption of other constituents in the chemical reactions, we were not able to identify hydroxyl absorption. A trial using Harvard's 21-foot concave grating (20,000 lines per inch) in the second order of a Paschen mounting showed that the emission from the discharge through water vapor was intense enough to be used with photo-multipliers (1P28).

# Hollow-Cathode Source Design for High Resolution Spectroscopic Studies with Small Samples

O. H. Arroe and J. E. Mack
*Department of Physics, University of Wisconsin, Madison, Wisconsin**

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A series of hollow-cathode tubes has evolved from the original Schüler type, for use at low temperature with valuable small samples (~10 mg). In the final tube assembly the light emerges with a divergence of *f*:3 through a 35-mm window. The cathode, of Al or Mg (or possibly Be) is clamp-sealed to the tube to be easily removable, yet in direct contact with liquid air. The tube has been used with a static rare gas supply as well as a conventional circulating system. Several quickly interchangeable sources have been used to make relative measurements of isotope shift with an uncertainty of about $2 \cdot 10^{-3}$.

THE requirements for a light source for the experimental spectroscopic study of hyperfine structure and isotope shift with separated isotope samples are the following:

1. A few milligrams of the sample must give a rich spectrum
2. Recovery of the sample must be feasible after use.
3. The thermal line width must be small.

The source we used at the start of our studies in 1947 was in principle a conventional liquid-air cooled Schüler tube with a removable aluminum cathode inserted in a taper joint inside the copper bottom of the vacuum tube (Fig. 1). For initimate contact, to give a good thermal conductivity, the joint was assembled after cooling the aluminum in liquid air and heating the copper to about 300°C. The anode was an oxidized iron tube, with an aluminum ring attached a few mm from the cathode. The iron anode was separated from the surrounding Inconel tube by a glass tube, which was sealed to the cathode with Picein just above a water jacket. The circulating carrier gas came down through a liquid-air cooled charcoal trap and reached the discharge through four canals in the aluminum.

Although this source was used successfully in the study of $_{30}Zn^{67}$,[1] a progressive alteration in the shape of the taper joint after the cup had been changed a few times, lowering the heat conductivity and consequently increasing the Doppler width, led to a change in design as shown in Fig. 2. Here the cathode cup was clamp-sealed to the Inconel tube so as to be in direct contact with the liquid air. The new clamp seal was vacuum tight, and made it still possible to use the thin Inconel tube to keep down the liquid air consumption. For convenience in the disassembly process, the wax seal between the glass part and the cathode was replaced by a ground glass joint. The carrier gas was not circulated through the discharge, but this alteration made no apparent change in the intensity or in the purity of the discharge.

Because with any cathode one might want to study lines inconveniently close to lines characteristic of the cathode substance, it is advantageous to have available cathodes of more than one substance. We have found both magnesium† and aluminum satisfactory for cathodes, and have obtained one of beryllium, thus far unused. As might be expected from the relative rates of deposition by sputtering,[2] the magnesium is superior to the aluminum in that it takes longer time to suppress the spectrum by covering the exposed surface of the sample, although the aluminum is preferable in general for the relative weakness of its own lines and the

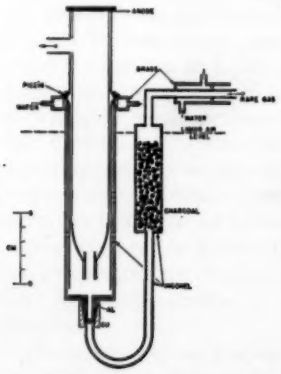


FIG. 1. Schüler tube with charcoal trap inlet.

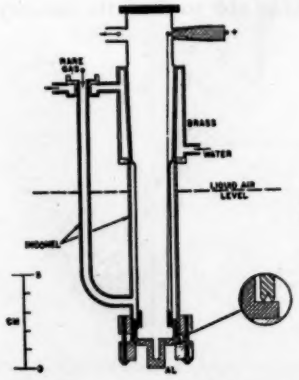


FIG. 2. Tube with removable clamp-sealed cathode. Insert: detail of clamp seal.

* Partly supported by Navy Contract N7onr-285TO#1, NR 019 107.

† Donated by the Dow Chemical Company, Midland, Michigan, through A. MacDonald.

[1] O. H. Arroe, Phys. Rev. 74, 1263A (1948).

[2] A. Güntherschulze, Zeits. f. Physik 38, 575 (1926).

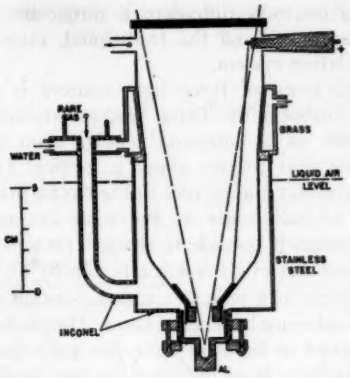


FIG. 3. Large clamp-sealed wide-beam tube.

chemical stability of its surface in the presence of atmospheric moisture.

The divergence of the light emanating from these sources was about $f$:6. The predispersion instrument used with these two light sources was a regular Hilger constant-deviation spectrometer with collimator and camera lenses of 30 mm diameter and 55 cm focal length. The Fabry-Perot interferometer was placed in the parallel beam between the collimator lens and the prism.

Experience has shown that a discharge about 5 mm in diameter and about 10 mm long is convenient for work with a small quantity of material. Since an image approximately 15 mm high (i.e., a linear magnification of 3 from the condensing lens) was needed on the photographic plates to give a sufficient number of interference orders, the $f$:18 lens system of the spectrometer was just filled by this light source. This system was used in the study of $_{34}Se^{77}$.[3]

There became available to us in 1948 a special Hilger constant deviation spectrometer‡ with lenses 58 mm in diameter, a collimator of 55 cm focal length, and cameras of focal length 23 cm, 55 cm, and 125 cm. To enable us to use this fast instrument, it was necessary to increase the relative aperture of the light source, which was done first by simply increasing the diameter without changing the over-all length (Fig. 3). This source was rather unstable, and was subject to frequent small leaks in the joint when cooled in liquid air, because of the increased dimensions. It was soon replaced by the source we are now using (Fig. 4), several of which have been in highly satisfactory use for some time, for instance in the study of $_{40}Zr^{91}$ [4], $_{52}Te^{6}$, $_{56}Ba^{6}$, and $_{42}Mo$. In this, the diameter is the same as in earlier ones and the length has been decreased to give a divergence of $f$:3, with the light emerging up through a glass or quartz window 35 mm in diameter. The glass part is designed with a sleeve to deliver the carrier gas down into the neighborhood of the discharge and to prevent ions from striking any metal other than the electrodes. The two brass water-tubes extending vertically past the window serve as an optical bench for a condensing lens. The source is surrounded by a quadruple-walled can, supplemented by several radiation shields of polished stainless steel, which makes it feasible to immerse the cathode in liquid air to a depth as great as 10 cm. Thermal insulation of the cathode from the rest of the tube is achieved by letting it protrude below the can, joined to it only by the 25-mm diameter Inconel tube, of which 1 cm length is turned down to ½ mm in thickness. Although Inconel is no lower in thermal conductivity than 18–8 stainless steel, it is supposed to have preferable mechanical properties. Liquid air is boiled away at the rate of somewhat less than one-half liter per hour in keeping the cathode cold. The screws effecting the clamp seal are brass, with relative lengths calculated for compensation in expansion against the other metals.

A simpler, somewhat similar tube has been described[7] in which the cathode is cemented to the inner-half of a glass joint.

Our source has been used equally well in two kinds of gas supply system. One is a circulating system (Fig. 5) in which the circulation is maintained by a mercury diffusion pump. Two liquid-air cooled traps, one of them charcoal-filled, remove the last impurities from the system. The impurities may be from any of three sources: vapors not removed by the forepump, impurities in the carrier gas, and impurities given off by the isotope sample (usually an inorganic compound) in the first few minutes after the initiation of the discharge. Two carrier gas supplies are placed in the system, from either of which the gas can be admitted

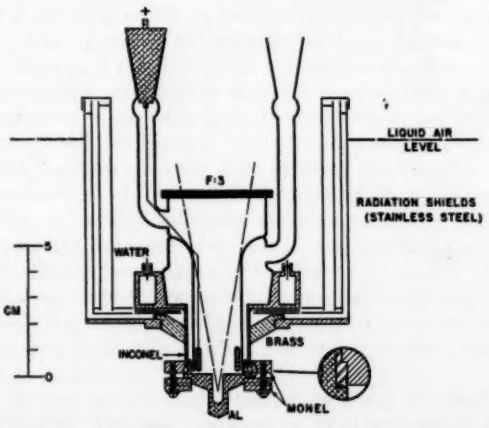


FIG. 4. Clamp-sealed wide-beam tube in current use. Insert: detail of clamp seal and tapped ring.

[3] J. E. Mack and O. H. Arroe, Phys. Rev. 76, 173A (1949).
‡ Bought with funds granted by the University research committee.,
[4] O. H. Arroe and J. E. Mack, Phys. Rev. 76, 873 (1948).
[5] J. E. Mack and O. H. Arroe, Phys. Rev. 76, 1002 (1949).
[6] O. H. Arroe, Phys. Rev. 77, 745A (1950).
[7] H. Kopfermann, H. Krüger, and H. Öhlmann, Zeits. f. Physik 126, 760 (1949).

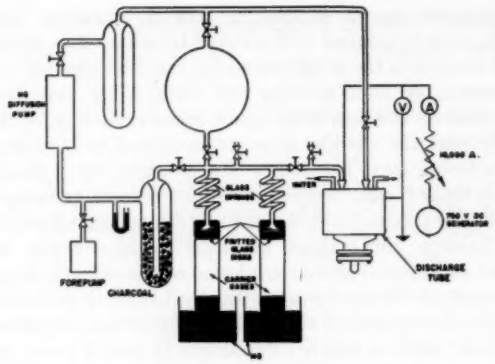


FIG. 5. Circulating system.

by contact between two fritted glass disks, which are permeable for gases but not for mercury.[8] The whole circulation system, including the hollow cathode, is mounted on a portable frame.

In the other system we succeeded in replacing the circulation with a simple rare-gas filling system, consisting of only a gas container with a valve and a liquid-air cooled charcoal trap, through which the gas passes before entering the light source. With a tight system, no intensity difference is noticeable between this simple system and the traditional, more complicated circulation system.

A special array of three light sources is used for studies of isotope shift. Three sources are mounted at 60° intervals on a horizontal circle, upon a sturdy metal frame that rotates about a vertical axis. Two manifolds connect the sources to the circulation system by means of ball joints in line with the axis. This mounting makes it possible to change from one isotope sample to another in a few seconds, simply by rotating one light source at a time to a source position carefully adjusted in advance by a set of stops. The photographic plate is moved in its own plane perpendicular to the lines, to get lines from different isotopes immediately adjacent to one another, making it possible to measure an isotope shift considerably smaller than the instrument can resolve. For instance, in barium, the Doppler width in liquid air is about $12\times10^{-3}$ cm$^{-1}$ and the limit of the instrumental resolution of the 40-mm etalon about $4.5\times10^{-3}$ cm$^{-1}$, yet in a representative line a shift of about $1.5\times10^{-3}$ cm$^{-1}$ has been detected between two isotope samples, with an uncertainty of about $0.4\times10^{-3}$ cm$^{-1}$. A somewhat similar procedure has been used independently by Koch and Rasmussen.[9]

[8] E. Rasmussen, Kgl. Danske Vid. Sels. Math.-fys. Medd. **18**, No. 5 (1940).

[9] J. Koch and E. Rasmussen, Phys. Rev. **76**, 1417 (1949).

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# Fluorescence Studies of Some Simple Benzene Derivatives in the Near Ultraviolet. I. Fluorobenzene and Chlorobenzene*,†

ARNOLD M. BASS‡ AND H. SPONER
*Department of Physics, Duke University, Durham, North Carolina*

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The vapor phase fluorescence has been studied in the near ultraviolet for a number of benzene mono-derivatives. The fluorescence was excited at vapor pressures of about 10 to 20 mm Hg using in most cases light from condensed sparks. The spark electrodes were selected so that the excitation of the molecules by the light was mainly into the strong absorption region near the O,O band. The fluorescence spectra were photographed on a Bausch and Lomb medium quartz spectrograph using slit widths ranging from 10 to 300μ. The exposure times on Eastman II-O plates were from 6 to 120 hr. The compounds studied are benzene, chlorobenzene, and fluorobenzene. Chlorobenzene was irradiated by light from Cu, Ni, and Bi sparks and the Hg arc, but in no case could any fluorescence be detected. Fluorobenzene, when excited by a tin spark, gives rise to a fluorescence spectrum of about 90 bands in the region 2640–3000A. Prominent ground state fundamental vibrations are found to occur which agree with values from Raman effect measurements. The analysis of the fluorescence spectrum of fluorobenzene is in agreement with that of the absorption spectrum, i.e., the first electronic transition (singlet terms) is an $A_1 \leftrightarrow B_1$, with the molecules having $C_{2v}$ symmetry. Carbon ring vibrations and hydrogen vibrations appear excited in the fluorescence spectrum. Several progressions of totally symmetric vibrations are identified, and a number of bands are explained as combinations of fundamental vibrations. Symmetry assignments are suggested for some of the fundamental vibrations.

## INTRODUCTION

THE fluorescence of organic compounds has been studied for some time. However, the fluorescence spectra of relatively few substances in the vapor phase are known. In the case of substituted benzenes, detailed analyses have been given only for the fluorescence spectra of benzene[1–6] and some of its deuterated derivatives[7,8] and for aniline.[9,10] Incomplete fluorescence measurements have been reported for fluorobenzene[11] and toluene.[12]

The fluorescence process involves transition from various vibrational levels of an excited electronic state to various vibration levels of some lower electronic state. If on absorption of monochromatic light the molecules are raised to a certain vibrational level of an upper electronic state, and if the gas pressures are sufficiently low so that practically no collisions occur during the lifetime of the excited molecules, the light emitted by these molecules will show the so-called resonance fluorescence spectrum. However, if the pressure is sufficiently high, the excited molecules lose vibrational energy by collisions and approach a distribution of vibrational levels in the excited state resembling the normal temperature distribution.

The least complicated fluorescence spectrum will be obtained if the exciting light is a spectral line which falls into the strong absorption region close to the head of the O,O band of the substance under investigation. As indicated above, for low pressures one would then obtain only transitions from the vibrationless level of the upper state to vibrational levels of the ground electronic state. If the light absorbed reaches a higher vibrational level and the pressure is very low, the fluorescence spectrum is again simple containing predominantly transitions from the particular excited level. The spectrum will become complicated with rising pressure because, even at moderate pressures, collisions will distribute the vibrational excitation energy over a range of oscillation levels in the upper electronic state. If a higher pressure (a few cm) is chosen, the energy distribution of the excited state tends to go over into a Boltzmann distribution of the oscillation states. The Boltzmann distribution may be reached also if the excitation takes place in the O,O transition, but in this case it will be reached only at still higher pressures. This must be the case since to reach the temperature equilibrium of the oscillatory system in an excited state, a strongly vibrating molecule must lose energy under the influence of collisions, and it will do so by practically any impact. To achieve the same when starting from a non-oscillating excited molecule, the oscillatory system has to gain energy by collisions with energy-rich molecules which, according to the circumstances, are rare.

In the current study, fluorescence was obtained at relatively high gas pressures. The absorption of the chosen molecules had been investigated before[13,14] and,

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† This investigation was assisted by the ONR under Contract N6ori-107, Task Order I, with Duke University.
‡ Present address: Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[1] G. B. Kistiakowsky and M. Nelles, Phys. Rev. **41**, 595 (1932).
[2] G. R. Cuthbertson and G. B. Kistiakowsky, J. Chem. Phys. **4**, 9 (1936).
[3] C. K. Ingold and C. L. Wilson, J. Chem. Soc. 1941 (1936).
[4] C. L. Wilson, J. Chem. Soc., 1210 (1936).
[5] H. Sponer, G. Nordheim, A. L. Sklar, and E. Teller, J. Chem. Phys. **7**, 207 (1939).
[6] F. M. Garforth and C. K. Ingold, J. Chem. Soc., 427 (1948).
[7] F. M. Garforth and C. K. Ingold, J. Chem. Soc., 440 (1948).
[8] A. P. Best, C. K. Ingold, and C. L. Wilson, J. Chem. Soc., 456 (1948).
[9] A. Vartanian, Bull. acad. sci. U.R.S.S. Sér. phys. **3**, 341 (1938).
[10] A. Vartanian, J. Phys. U.S.S.R. **1**, 213 (1939).
[11] M. W. Monypeny and A. Russell, J. Chem. Soc. 2436 (1929).
[12] J. K. Marsh, J. Chem. Soc. **123**, 3315 (1923).
[13] S. H. Wollman, J. Chem. Phys. **14**, 123 (1946).
[14] H. Sponer and S. H. Wollman, J. Chem. Phys. **9**, 816 (1941).

together with the fluorescence observations, an extension of the analysis of their electronic spectra was obtained, as will be discussed below.

## EXPERIMENTAL DETAILS

In the substances studied, fluorescence was excited with light from a number of different sources. In each case, a light source was chosen which would excite the O,O absorption band as strongly as possible while at the same time it would excite to a much lesser degree a few other bands of the absorption spectrum. For most of the cases, light from condensed sparks was used. The electrodes were selected so that there were strong lines in the spark spectra within one angstrom unit toward the long wave side of the band head since the absorption bands studied degrade to the red. The electrodes were clamped in a spark stand to which was coupled a variable speed drive motor. Thus, by adjusting the input voltage to the motor, the electrodes could be fed at a rate to compensate for the burning away of the electrode material. It was found advantageous to direct a stream of air at the spark gap. The spark was enclosed in a hood which was connected to a ventilating fan.

The spark electrodes were placed in the usual type of circuit for the production of condensed sparks.[15] For the excitation of the benzene fluorescence and for the first part of the study of fluorobenzene, a high voltage transformer rated at 17,600 v and 10.4 kw was used in combination with 0.05 $\mu$f of capacity in parallel with the spark gap. The operating conditions of this circuit were such that spark was excited at a voltage of about 4500 v and a power of about 0.9 kw. For the final study of fluorobenzene and for the later work on other compounds, a specially designed transformer (built by the Thordarson Electric Manufacturing Company) rated at 10,000 v and 1 kw was used. With this transformer the sparks were excited at the full rating of the transformer and with a capacity§ of 0.025 $\mu$f.

The light from the spark was passed through suitable filters on to the vapor under investigation (Fig. 1). Highly purified samples of the substances‖ studied were distilled in vacuum into a quartz vessel of common design for fluorescence experiments, great care being taken to eliminate so far as possible foreign gases which tend to change the appearance of the fluorescence. The pressure of the vapor exposed to the exciting light was determined by controlling the temperature of the body substance in the side arm of the fluorescence vessel. For work at higher vapor pressures, the cell and side arm were placed in individually controlled furnaces.

In order to reduce the amount of photo-decomposition in the vapor, and in order to determine definitely the line of the exciting spectrum which is most active in producing the fluorescence, a series of short wave-length cut-off filters was developed using organic compounds.[16] These filters were used in combination with glass filters (Corning filters No. 9863 "Red Purple Corex A" and No. 791 "96% Silica UV Transmitting") and were placed between the spark source and the entrance window of the fluorescence cell. To isolate the exciting line for each compound, a series of exposures was made using filters with different concentrations of the filter solution. Each of these exposures was made with wide slits and short exposure times. The resulting spectra were quite diffuse. It was observed that as the concentration of the filter solution was increased, thus shifting the cut-off wave-length toward the red, the character of the fluorescence was essentially unchanged. At a certain concentration, however, it was found that the fluorescence disappeared, thus indicating that the filter solution was absorbing the active line of the exciting spectrum.

The fluorescent light was observed at right angles to the incident beam and the spectra were photographed with a Bausch and Lomb medium quartz spectrograph. The slit widths used ranged from 10 to 300 $\mu$ and exposure times, on Eastman II-O plates, ranged from 120 to 6 hr. In order to time the exposures, a photo-tube (RCA tube 918) was connected through a one-stage amplifier¶ to a time meter, measuring the duration of the illumination. The photo-tube was activated by light passing through the quartz absorption-fluorescence cell, and the action of the circuit was such that the clock was in operation as long as the light from the spark was passing through the cell.

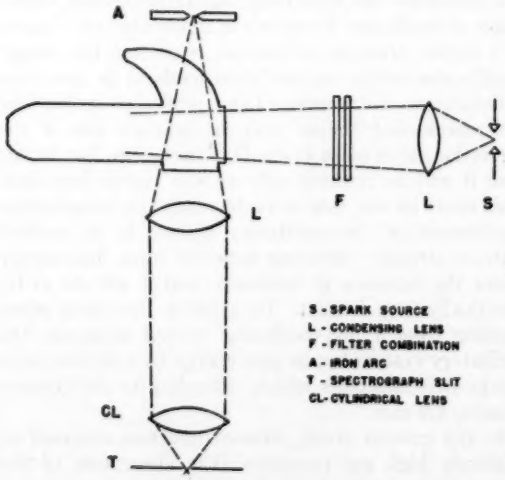


FIG. 1. Optical system.

[15] W. R. Brode, *Chemical Spectroscopy* (John Wiley and Sons, Inc., New York, 1943), second edition.

§ We are indebted to the Electrical Engineering Department of Duke University for the loan of the capacitors used in these experiments.

‖ We are very grateful to Dr. E. J. Hackney of the Chemistry Department of Duke University for supplying us with these samples.

[16] A. M. Bass, J. Opt. Soc. Am. 38, 977 (1948).

¶ We are grateful to Mr. Frank Trippe for designing and constructing this amplifier.

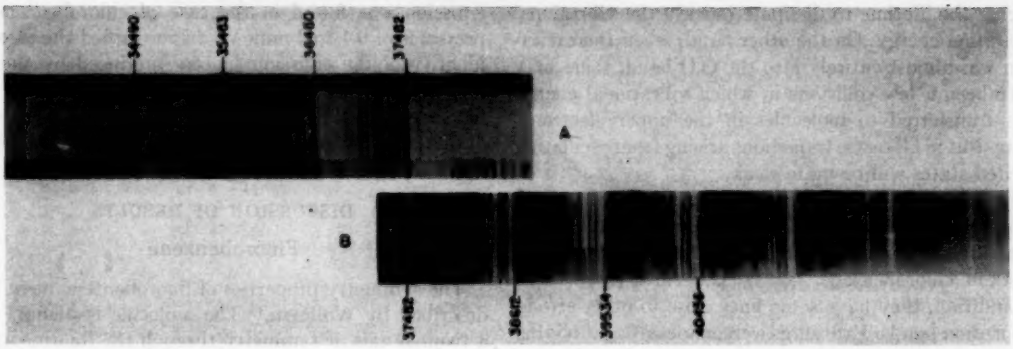


FIG. 2. A. Fluorescence spectrum of benzene vapor (excited by Mn spark, Corning No. 791 filter, vapor pressure 20 mm). B. Absorption spectrum of benzene (Hilger medium quartz spectrograph, vapor pressure 20 mm).

Measurements were made by comparison with the iron arc spectrum.

## EXPERIMENTAL RESULTS

### Benzene

The fluorescence spectrum of benzene is well known.[1–4,17,18] It was decided to re-photograph the benzene fluorescence spectrum as a check on the operation of our system. A manganese spark, which has a fairly strong line at 2589.7A, very close to the strong absorption band $A_0$ in benzene[5] at 2588.9A, was used as the exciting source. A very intense fluorescence was observed for a vapor pressure of 25 mm. The intense bands were measured and were found to be in close agreement with the results published by Ingold and Wilson[3] for the high pressure fluorescence of benzene. A photograph is included here together with the absorption spectrum (taken with about the same dispersion) because a direct comparison of the two spectra is instructive.

### Fluorobenzene and Chlorobenzene

The fluorescence of fluorobenzene was excited with light from a tin spark in which a line of medium intensity appears[19] at 2643.6A, very close to the fluorobenzene O,O band[18] at 2643.4A (37818.8 $cm^{-1}$). Vapor pressures were varied from 2 to 20 mm. Figure 3B shows the discrete spectrum that was obtained at a vapor pressure of 12 mm. The spectrum extends from about 37800 to 33300 $cm^{-1}$ (2645–3000A) and consists of 90 bands which degrade to the red. Table I lists the bands as measured in the fluorobenzene spectrum along with the intensities and probable assignments. The intensities were estimated visually according to the following scale: s—strong, ms—medium to strong, m—medium, mw—medium to weak, w—weak, vw—very weak; d—diffuse, vd—very diffuse; b—broad, vb—very broad. In the assignment column the number to the left of the comma gives the vibrational level of the lower electronic state, and the number to the right of the comma gives the vibrational level of the upper state involved in the transition. Numbers with negative signs to the right of the comma refer to $v,v$ transitions. Assignments for which there may be some doubt are enclosed in parentheses.

In addition to tin, sparks of Ni, Mn, Fe, and Zn, and a mercury arc were also used as exciting sources. In each case, the fluorescence obtained was weaker than noted, but the spectrum was essentially the same as for tin excitation. Figure 3A shows the fluorescence excited by a manganese spark, and the essential similarity to the spectrum excited by the tin spectrum is easily seen. The fluorescence spectrum studied in this research is much richer in bands than the one reported by Monypeny and Russell,[11] who used an Hg arc as exciting source.

The bands collected in Table I were measured from plates taken under various conditions, i.e., with filter solutions of different concentrations and also with the Corning No. 791 filter alone. It is therefore quite probable that in several exposures some excitation took place into vibrational levels of the upper electronic state, caused particularly through the strong spark lines at 2594.4 and 2571.6A which happen to almost coincide with two fairly strong absorption bands (2594.6 and 2573.1A). However, the aspect of the fluorescence spectrum was essentially the same as when, by using appropriate filters, the excitation was primarily into the O,O band. The spectrum always consisted mainly of bands arising from the zero vibrational level of the upper state. This is understandable since the lifetimes of the first excited states (singlet states) in the simple mono-derivatives of benzene are of the order $10^{-6}$ to $10^{-7}$ sec. Thus, at the applied pressures of 10 to 20 mm there were enough collisions

[17] P. Pringsheim and A. L. Reimann, Zeits. f. Physik **29**, 115 (1924).
[18] A. L. Reimann, Ann. d. Physik **80**, 43 (1926).
[19] H. Kayser and R. Ritschl, *Tabelle der Hauptlinien der Linienspektren aller Elemente* (Verlag Julius Springer, Berlin, 1939), second edition.

during the lifetime to dissipate quickly the vibrational excitation energy. On the other hand, when the excitation was almost entirely into the O,O band, there may have been a few collisions in which vibrational energy was transferred to molecules in the upper electronic state. But in all cases, transitions arising from oscillating excited states will be quite weak.

In attempting to excite the fluorescence of chlorobenzene, sparks of Cu, Bi, Ni, and the mercury arc were used since these sources have lines near the O,O band in chlorobenzene[14] at 37052.0 $cm^{-1}$ (2698.11A). In addition, they have some lines close to other strong absorption bands. Exposures were made with slit widths ranging from 100 to 250 $\mu$, for periods of 7 to 50 hr., and over a vapor pressure range of 2.8 to 12 mm. In no case could any trace of fluorescence be observed.

It is interesting to note these same compounds have been studied by Schüler and Woeldike[20–22] with respect to their emission spectra as excited through electron impact in the positive column of a hollow cathode discharge. It was found that a discrete emission spectrum could be observed in the ultraviolet for benzene and fluorobenzene. On the other hand, no ultraviolet emission was found in the case of chlorobenzene for pressures of 0.1 to 2 mm. We have verified the essential identity of the emission spectra produced by the two different methods of excitation (electron impact and light excitation) in the case of fluorobenzene by comparing the measurements presented with those made by Schüler.[23]

## DISCUSSION OF RESULTS

### Fluorobenzene

The symmetry properties of fluorobenzene have been described by Wollman.[13] The molecule is planar, with a twofold axis of symmetry through the fluorine atom, and belongs to the symmetry class $C_{2v}$. From the work of Wollman, we know that the spectrum which is observed in the near ultraviolet arises from an allowed electronic transition between the totally symmetric ground state ($A_1$) and a non-totally symmetric excited state ($B_1$).

As mentioned, we will expect that the simplest fluorescence spectrum will occur, if the excitation performed by monochromatic light be directly into the O,O band. In such a case, we would expect to observe

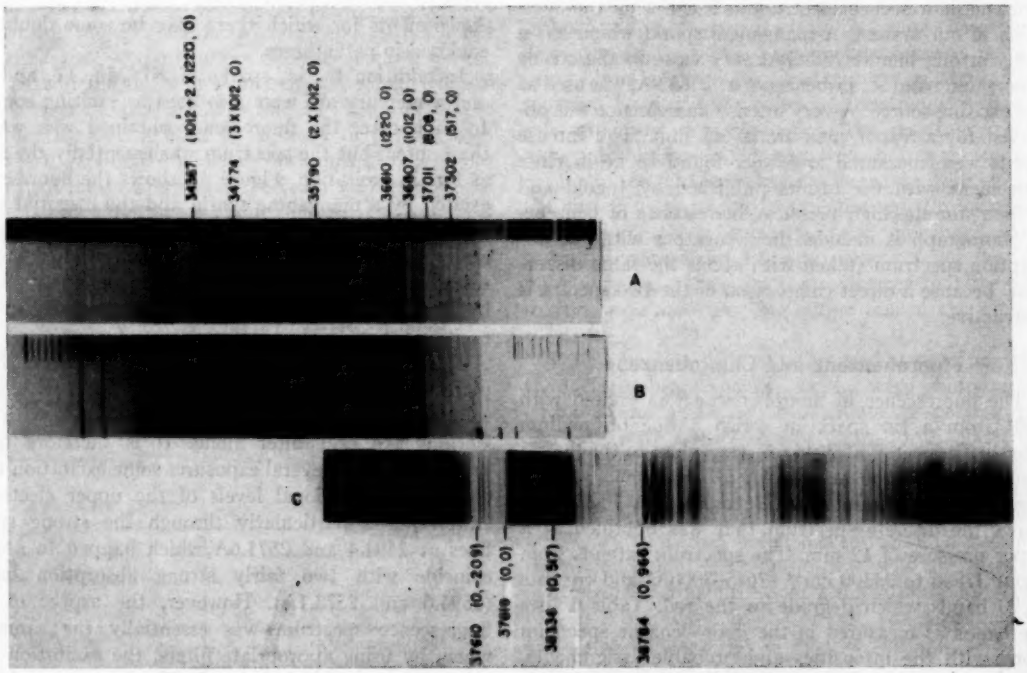


FIG. 3. Fluorescence spectrum of fluorobenzene vapor (A excited by Mn spark, Corning No. 9863 filter, exposure 20 hr., vapor pressure 16 mm; B excited by Sn spark, Corning No. 791 filter, exposure 50 hr., vapor pressure 12 mm) and absorption spectrum for comparison (taken by S. H. Wollman, reference 13, in first order of a 3-m grating, vapor pressure 4 mm).

[20] H. Schüler and A. Woeldike, Physik. Zeits. 42, 390 (1941).
[21] A. Woeldike, Zeits. f. Naturforschung 1, 566 (1946).
[22] H. Schüler, Zeits. f. Naturforschung 2a, 556 (1947).
[23] Private communication to H. Sponer.

TABLE I. Fluorescence bands of fluorobenzene.

| Wave-length Å | Wave number cm$^{-1}$ | Int. | Separation from O,O 37819 cm$^{-1}$ | Assignment |
|---|---|---|---|---|
| 2645.9 | 37783 | w, vd | 36 | (752, 779–67); (1069, 2×517); (808, 779) |
| 47.8 | 756 | w, b | 63 | 0, −67; (824, 762) |
| 51.3 | 706 | w, vd | 113 | (824, 779–67) |
| 52.8 | 685 | w, b | 134 | 0, −2×67 |
| 54.3 | 664 | vw | 155 | (673, 517) |
| 56.9 | 627 | mw | 192 | 0, −192; (2×612, 2×517) |
| 65.5 | 505 | w, d | 314 | 824, 517 |
| 69.3 | 452 | vw, b | 367 | (367, 0) |
| 72.4 | 408 | m, d | 411 | 411, 0 |
| 77.7 | 334 | vw | 485 | (2×241, 0) |
| 80.0 | 302 | m | 517 | 517, 0 |
| 84.0 | 247 | w | 572 | |
| 85.1 | 232 | m | 587 | 517, −67 |
| 86.9 | 207 | m | 612 | 612, 0 |
| 90.0 | 164 | m | 655 | 517, −2×67; (241+411, 0) |
| 91.3 | 146 | m | 673 | 673, 0 |
| 92.8 | 125 | mw | 694 | (1220, 517) |
| 94.6 | 100 | ms | 719 | 411+824, 517; (3×411, 517) |
| 95.7 | 085 | mw | 734 | (2×367, 0) |
| 97.0 | 067 | mw | 752 | (752, 0); (241+517, 0) |
| 2701.1 | 011 | s | 808 | 808, 0 |
| 02.3 | 36995 | s | 824 | 824, 0 |
| 06.1 | 941 | m | 878 | 808, −67 |
| 2711.9 | 36864 | w | 955 | 808, −2×67 |
| 15.6 | 813 | m | 1006 | (1006, 0); (2×500, 0); 2×241+517, 0 |
| 16.2 | 807 | s | 1012 | 1012, 0 |
| 17.4 | 789 | s | 1030 | 1030, 0 |
| 18.2 | 778 | s | 1041 | 2×517, 0; (241+808, 0) |
| 20.3 | 750 | ms | 1069 | (1069, 0); (241+824, 0) |
| 22.8 | 716 | mw | 1103 | 2×241+612, 0 |
| 23.8 | 703 | w | 1116 | (884+1012, 779) |
| 25.2 | 684 | m | 1135 | 517+612, 0; (2×824, 517) |
| 26.5 | 666 | w | 1153 | 1153, 0 |
| 28.4 | 641 | w | 1178 | |
| 30.7 | 610 | s | 1209 | 1220, 0 |
| 33.0 | 579 | s | 1240 | 2×612, 0 |
| 33.7 | 570 | s | 1249 | (241+1012, 0) |
| 35.5 | 546 | vw | 1273 | (241+1030, 0) |
| 36.1 | 538 | vw | 1281 | 808+2×241, 0 |
| 37.6 | 518 | mw | 1301 | (1301, 0); 824+2×241, 0 |
| 39.0 | 499 | mw | 1320 | 517+808, 0 |
| 42.4 | 454 | w | 1365 | (1365, 0) |
| 43.2 | 443 | w | 1376 | (367+1012, 0) |
| 43.9 | 434 | w | 1385 | (367+1030, 0) |
| 46.9 | 394 | m | 1425 | 411+1012, 0; 612+808, 0 |
| 47.7 | 383 | ms | 1436 | (612+824, 0) |
| 52.6 | 319 | w | 1500 | 1500, 0; (2×752, 0) |
| 2754.5 | 36294 | m | 1525 | 517+1012, 0 |
| 55.6 | 279 | m | 1540 | 517+1030, 0 |
| 62.3 | 191 | m | 1628 | 808+824, 0; (2×808, 0); (612+1012, 0) |

TABLE I (*continued*).

| Wave-length Å | Wave number cm$^{-1}$ | Int. | Separation from O,O 37819 cm$^{-1}$ | Assignment |
|---|---|---|---|---|
| 63.6 | 174 | mw | 1645 | 2×824, 0; (612+1030, 0) |
| 64.6 | 161 | mw | 1658 | |
| 68.8 | 106 | mw, d | 1713 | (411+1301, 0) |
| 69.7 | 094 | mw | 1725 | |
| 70.3 | 087 | mw | 1732 | 517+1220, 0 |
| 71.4 | 072 | w | 1747 | 517+2×612, 0; 1012+2×367, 0 |
| 76.8 | 002 | ms | 1817 | 808+1012, 0; (517+1301, 0) |
| 81.8 | 35937 | w | 1882 | (808+1069, 0); (517+1365, 0) |
| 83.9 | 910 | m | 1909 | (752+1153, 0) |
| 84.6 | 901 | w | 1918 | (612+1301, 0); (411+2×752, 0) |
| 87.1 | 869 | w, d | 1950 | 808+1153, 0; (411+517+1012, 0) |
| 89.2 | 842 | w | 1977 | 824+1153, 0 |
| 92.1 | 805 | ms | 2014 | 2×1006, 0 |
| 92.8 | 796 | ms | 2023 | 2×1012, 0; 808+1220, 0 |
| 94.3 | 777 | s | 2042 | 1012+1030, 0; 824+1220, 0 |
| 95.0 | 768 | ms | 2052 | 2×1030, 0; 1012+2×517, 0 |
| 97.0 | 742 | w, d | 2077 | 241+808+1030, 0; (1012+1069, 0) |
| 99.5 | 710 | w | 2109 | (808+1301, 0); (1030+1069, 0); (367+517+1220, 0) |
| 2804.5 | 646 | w | 2173 | 1012+1153, 0; 517+2×824, 0; (808+1365, 0) |
| 07.5 | 608 | m | 2211 | (241+752+1220, 0) |
| 2808.9 | 35591 | mw | 2228 | 1012+1220, 0; 1012+2×612, 0 |
| 10.0 | 577 | m | 2242 | 1030+1220, 0 |
| 10.7 | 568 | m | 2251 | 1220+2×517, 0; 1030+2×612, 0; (612+808+824, 0) |
| 12.5 | 545 | m, b | 2274 | |
| 26.1 | 374 | mw, d | 2445 | 2×1220, 0; 824+2×808, 0 |
| 33.2 | 285 | w | 2534 | 517+2×1012, 0; (1030+2×752, 0) |
| 43.5 | 158 | w | 2661 | 1012+2×824, 0; 808+824+1030, 0; 411+1030+1220, 0; (612+2×1030, 0) |
| 46.9 | 116 | w | 2703 | (1069+2×824, 0) |
| 57.6 | 34984 | w, b | 2835 | 808+2×1012, 0; 2×808+1220, 0 |
| 74.9 | 774 | mw, vd, b | 3045 | 3×1012, 0; 808+1012+1220, 0 |
| 80.8 | 702 | vw | 3117 | 808+2×1153, 0; (517+2×1301, 0) |
| 86.7 | 632 | w | 3187 | (3187, 0); (752+2×1220, 0) |
| 91.7 | 572 | mw, d | 3247 | 1220+2×1012, 0; 808+2×1220, 0 |
| 2908.9 | 367 | mw, d | 3452 | 1012+2×1220, 0 |
| 25.4 | 173 | w, d, b | 3646 | (3×1220, 0) |
| 36.2 | 048 | w | 3771 | (1030+1220+1500, 0) |
| 42.5 | 33975 | vw, vd, vb | 3844 | 808+3×1012, 0; 2×808+1012+1220, 0 |
| 60.3 | 771 | vw, d, b | 4048 | 4×1012, 0 |
| 78.5 | 570 | w, d, b | 4249 | (1069+3187, 0); (1220+2×1500, 0) |
| 96.3 | 370 | vw, vd, b | 4449 | |

a discrete spectrum extending to the long wave-length side of the O,O band. The O,O band may appear weakened as a result of reabsorption within the quartz vessel. In addition, there should be observed totally symmetric ($\alpha_1$) vibrations of the ground state; non-totally symmetric ($\alpha_2$, $\beta_1$, $\beta_2$) vibrations in 2,0 transitions, but with smaller intensity than the $\alpha_1$-vibrations; and $\alpha_2$- and $\beta_1$-vibrations in weaker 1,0 bands alone and combined with the various totally symmetric vibrations.

If, through irradiation with shorter wave-lengths, higher vibrational levels are excited together with the electronic transition the spectrum will become more complicated. In this case, there will occur $v,v$ transitions with $v>0$, and also transitions between various vibrational levels of the two electronic states. But these latter bands will probably be weakened by reabsorption and also as a result of the reduction of energy in the molecule through collisions of the second kind, as was discussed in the preceding section. The Franck-Condon principle is another factor of importance for the appearance of the spectrum.

It is seen from Table I that the O,O band does not appear in fluorescence, probably because of reabsorption in the quartz cell. Taking Wollman's[13] value of the O,O band, 37819 cm$^{-1}$, we have computed the separations of the measured fluorescence bands from the O,O band. These frequency differences are listed in the fourth column of Table I. The vibrations which are most strongly excited in the ground state have the frequencies: 411, 517, 612, 808, 824, 1012, 1030, 1069, and 1220 cm$^{-1}$. The fundamental ground state vibration frequencies which have been observed in fluorescence are collected in Table II, where symmetry assignments are given and where they are compared with the values obtained through other methods. Each of the strong totally symmetric vibrations is found to be excited in the ground state up to at least two quanta, and also in many combinations.

The 517- and 612-cm$^{-1}$ frequencies are explained in the same way as the corresponding frequencies (520 and 617 cm$^{-1}$) were explained in the ultraviolet absorption.[13] That is, these two frequencies arise from the 606 cm$^{-1}$ $\epsilon_g^+$-carbon vibration in benzene when the reduction in symmetry from $D_{6h}$ to $C_{2v}$ removes the degeneracy.

As in the case of absorption, there are found in the

1000-cm$^{-1}$ region two strong totally symmetric carbon vibrations of frequency 1012 and 1030 cm$^{-1}$, respectively (in absorption 1012 and 1027 cm$^{-1}$). Also, a band of medium intensity is observed at 1006 cm$^{-1}$ which probably corresponds to the 996,0 transition reported by Wollman. No definite explanation can be given for this band at present. It is unlikely that it represents the excitation of a totally symmetric carbon or hydrogen vibration. On the other hand, its intensity seems too high[24,25] for interpreting it as twofold excitation of a non-planar $\beta_2$ carbon vibration such as 2×500, following Kohlrausch and Wittek.[26]

The vibrational frequency 808 cm$^{-1}$ has been suggested before[26] as correlated with the carbon-fluorine valence vibration (813 cm$^{-1}$ in absorption[13] and 807 cm$^{-1}$ in Raman[26] giving a strongly polarized line). This value seems somewhat low in view of corresponding vibrational frequencies in some other fluorinated hydrocarbons.

The strong band of frequency 824 cm$^{-1}$ is to be correlated with the 831-cm$^{-1}$ vibration observed in the Raman effect[26] and the 829-cm$^{-1}$ vibration observed in ultraviolet absorption. Kohlrausch and Wittek assigned the symmetries $\alpha_2$ and $\beta_2$ to this vibration, assuming that it represents a close pair resulting from the splitting of the 850-cm$^{-1}$ $\epsilon_g^-$-out-of-plane hydrogen vibration in benzene. Wollman, on the other hand, believed this to be a totally symmetric vibration. From Table I, it is seen that the 824-cm$^{-1}$ band appears very strongly by itself and many times in combination with other vibrations to produce moderately intense bands. This would support the assignment of $\alpha_1$-symmetry made by Wollman for this vibration. The independence of the 824-cm$^{-1}$ vibration upon the substituent observed in Raman spectra points to a hydrogen vibration.

The pair of strong bands at 36610 and 36579 cm$^{-1}$, separated from the O,O band by 1209 and 1240 cm$^{-1}$, respectively, may represent an accidental degeneracy between the fundamental 1220-cm$^{-1}$ and the twice excited 612-cm$^{-1}$ vibrations. In fluorescence, there is evidence for the existence of the totally symmetric vibration frequency 1220 cm$^{-1}$ in the occurrence of the twice excited vibration at 35374 cm$^{-1}$ and also in a large number of combination bands. Furthermore, the 612-cm$^{-1}$ vibration of symmetry $\beta_1$ has, when twice excited, the frequency 1224 cm$^{-1}$ and symmetry $\alpha_1$. Thus, the conditions for "Fermi resonance"[27] (i.e., identical symmetry and close approach of energy levels) are fulfilled and may account for the marked shift of the bands. It should be noted that no such perturbation is reported in the ultraviolet absorption. There are bands at the same locations, but they were interpreted differently. Also Wollman observed actually a band distant by 1218 cm$^{-1}$ from the O,O band, but he lists also the alternate assignment 1012, −209 for this band. No such band could be found in fluorescence. Because of these ambiguities, the explanation of the two fluorescence bands as resulting from an accidental degeneracy must be considered as a possible, though not definite, interpretation. As to the nature of the 1220-cm$^{-1}$ band, a carbon vibration has been suggested by Kohlrausch and Wittek and a hydrogen vibration by Pitzer and Scott.[28] Neither the absorption nor the fluorescence measurements suggest a preference of one of the two interpretations.

No band is observed corresponding to the 240-cm$^{-1}$ vibration in ultraviolet absorption measurements and 241 cm$^{-1}$ in the Raman effect. However, although this frequency does not appear once excited alone, a band (37334) is observed which may be explained as the 2,0 transition of this vibration, and several bands fit combinations of 2×241 with totally symmetric vibrations. This would seem to support the view of Kohlrausch and Wittek that this vibration has symmetry $\beta_2$. They considered it a carbon vibration related to the 406$\epsilon_u^+$ in benzene. There are, however, two bands of moderate intensity which can best be accounted for by the 241-cm$^{-1}$ vibration once excited. These are: 37067 cm$^{-1}$ which may be associated with the transition 241+517,0; and 36570 cm$^{-1}$ from the transition 241+1012,0. Both

TABLE II. Ground state vibration frequencies in fluorobenzene.

| Raman Kohlrausch and Wittek[a] | Infra-red Lecomte[b] | Ultra-violet absorp-tion Woll-man[c] | This research | Symmetry Refer-ence a | Refer-ence c | This re-search |
|---|---|---|---|---|---|---|
| 241 (12, 0.83) | | 240 | (242) | $\beta_2$ | $\alpha_2$ | |
| 274 (00 ?) | | | | | | |
| 368 (00 ?) | | | (367) | $\beta_1$ | | |
| 407 (00 ?) | | | 411 | $\alpha_2$ | | $\alpha_2$ |
| 463 (0 ?) | | | | | | |
| 496 (2) | | | (500) | $\beta_2$ | | ($\beta_2$) |
| 519 (10, 0.60) | 518 | 520 | 517 | $\alpha_1$ | $\alpha_1$ | $\alpha_1$ |
| 612 (7, 0.92) | 610 | 617 | 612 | $\beta_1$ | $\beta_1$ | $\beta_1$ |
| | 680 | | (673) | $\alpha_2$ and $\beta_2$ | | ($\alpha_2$) |
| 759 (4, 0.54) | 750 | | (752) | $\beta_2$ | | |
| 807 (15, 0.12) | 802 | 813 | 808 | $\alpha_1$ | $\alpha_1$ | $\alpha_1$ |
| 831 (2) | | 829 | 824 | $\alpha_2$ and $\beta_2$ | $\alpha_1$ | $\alpha_1$ |
| 900(0 ?) | 895 | | | | | |
| 997 (8) | 997 | 996 | (1006) | | | |
| 1010 (15) (0.07) | | 1012 | 1012 | $\alpha_1$ | $\alpha_1$ | $\alpha_1$ |
| 1024 (8) | 1035 | 1027 | 1030 | $\alpha_1$ | $\alpha_1$ | $\alpha_1$ |
| 1068 (2) | | | 1069 | | | |
| 1157 (10, 0.65) | | 1157 | 1153 | $\alpha_1$ and $\beta_1$ | $\alpha_1$ | $\alpha_1$ |
| 1218 (9, 0.15) | 1202 | 1218 | 1220 | $\alpha_1$ | $\alpha_1$ | $\alpha_1$ |
| 1267 (0 ?) | | | 1273 | | | |
| 1295 (1/2, 0.70) | | | | | | |
| 1301 (1/2 ?) | | | 1301 | | | |
| 1370 (1/2) | | | (1365) | $\beta_1$ | | |
| 1496 (2) | | | 1500 | $\alpha_1$ | | |
| 1595 (6) (0.77) | | | | | | |
| 1603 (6) | | | | $\alpha_1$ and $\beta_1$ | | |
| 1626 (0) | | | (1628) | | | |
| 2618 (1) | | | | | | |
| 2985 (1/2) | | | | | | |
| 3027 (3) | | | | | | |
| 3072 (12b) (0.40) | | | | | | |
| 3084 (6) | | | | $\alpha_1$ | | |
| 3185 (4) | | | 3187 | | | |

[a] See reference 26.
[b] See reference 29.
[c] See reference 13.

[24] G. Herzberg and E. Teller, Zeits. f. physik. Chemie B21, 410 (1933).
[25] H. Sponer and E. Teller, Rev. Mod. Phys. 13, 75 (1941).
[26] K. W. F. Kohlrausch and H. Wittek, Monats. f. Chem. 74, 1 (1941).
[27] E. Fermi, Zeits. f. Physik 71, 250 (1931).
[28] K. S. Pitzer and D. W. Scott, J. Am. Chem. Soc. 65, 803 (1943).

bands occur also in absorption. If these assignments are correct, then the only way in which these bands can appear with their observed intensities is for the 241-cm$^{-1}$ vibration to have a symmetry other than $\beta_2$. Wollman has assigned the symmetry $\alpha_2$ to this vibration considering symmetry $\beta_1$ as less likely. His assignment would satisfy the necessary conditions for the two bands just mentioned above. However, Wollman observed the transition 240,0 in absorption which does not appear in fluorescence. The results obtained from fluorescence do not permit an unambiguous choice between the proposal of Kohlrausch and Wittek and that of Wollman regarding the symmetry of this vibration.

Lecomte[29] has observed a strong band of frequency about 680 cm$^{-1}$ in the infra-red absorption spectrum of fluorobenzene. This band is characteristic of the infra-red spectra of monosubstituted benzenes and occurs with only a small change in frequency from one compound to another. It was therefore interpreted as an hydrogen vibration. Lecomte reports that there are two possible explanations for this band, that is, it may be connected with either the $\alpha_{2u}$- or the $\beta_{2g}$-vibration in benzene, thus representing a $\beta_2$-vibration in fluorobenzene. Kohlrausch and Wittek, while they did not observe the vibration in the Raman spectrum, interpreted the infra-red band as a close pair having symmetries $\beta_2$ and $\alpha_2$. This pair, they believe, arises from the splitting of the degenerate $\varepsilon_u^+$ hydrogen vibration in benzene. We know that vibrations of symmetry $\beta_2$ cannot appear alone once excited in the fluorescence spectrum. But if the explanation of Kohlrausch and Wittek is correct, it should be possible to observe the $\alpha_2$-component of the pair. In the spectrum, as listed in Table I, there is a band of medium intensity at 37146 cm$^{-1}$, separated from the O,O band by 673 cm$^{-1}$. It is possible to explain this band also as the transition 612+1030,966. But such an alternative should give rise to a band with much smaller intensity than actually is observed. The band at 36454 cm$^{-1}$ for which the tentative assignment 1365,0 is given in Table I is probably too high in wave number to account for a transition 2×673,0. The evidence for the presence of a fundamental vibration of frequency 673 cm$^{-1}$ must be regarded as incomplete.

Wollman has found in the ultraviolet absorption spectrum difference frequencies of 20, 67, 98, 172, and 209 cm$^{-1}$ resulting from $v,v$ transitions. In the fluorescence spectrum we also find bands with separations from the O,O band in the same frequency range. The most prominent is the difference frequency 67 cm$^{-1}$ which, in addition, occurs superposed on some of the strong totally symmetric vibrations, as in the case of absorption. No assignment is suggested for this difference frequency.

Some faint bands are present which indicate that emissions occur from excited states possessing quanta of vibrational energy. This is understandable since, as mentioned before, these bands were observed with filters which permit the strong spark lines of Sn at 2594.4A and possibly 2571.1A to enter the fluorescence cell. These lines will be absorbed because of their very close proximity to the fairly strong absorption bands 2594.6A and 2573.1A. As discussed above, most of the excited states which are involved will lose their vibrational energy by collisions, thereby giving rise to a stronger population of the non-oscillating excited state. Only a few will be able to dispose of their energy directly by light emission through transitions from the vibrational levels of the upper electronic state to the vibrational levels of the ground state. It may be noted that no bands have been found corresponding to transitions from vibration levels in the upper state to the vibrationless ground state. This is explained by a process of reabsorption of these bands taking place in the fluorescence cell. The observed bands arising from emission by vibrating molecules involve mainly the vibrations 517, 762, and 779 cm$^{-1}$ in the upper state. The frequencies 762 and 779 cm$^{-1}$ correspond to totally symmetric vibrations and so may combine with all ground state vibrations except those of symmetry $\beta_2$. The 517-cm$^{-1}$ vibration in the upper state has symmetry $\beta_1$ which means that transitions from this level will probably give rise to bands of lower intensity than the others; these transitions are most likely to involve in the ground state totally symmetric vibrations or once excited $\beta_1$-vibrations. Transitions to once excited $\beta_2$-vibration levels are permitted, but with low intensity, while transitions from $\beta_1$ to $\alpha_2$ are forbidden.

### Chlorobenzene

As mentioned in the "Results" section, no fluorescence spectrum of chlorobenzene was obtained. This should be the case if the fluorescence yield is $\leqq 10^{-4}$, i.e., if the natural lifetime of the excited state is reduced by a factor $10^4$ or more by external or internal influences. A rough estimate of the natural lifetime from the $f$-value for the first electronic transition (singlet) in chlorobenzene gives a value of about $10^{-6}$ sec.; therefore, the actual lifetime must have been $\leqq 10^{-10}$ sec. We mention that no diffuseness of the ultraviolet absorption spectrum is observed for low lying vibrational levels of the excited electronic state. However, this is not to be expected if the lifetime is not shortened by much more than a factor of $10^4$.

The question arises then whether the abbreviation of the natural lifetime is caused by the external effects of quenching impacts, i.e., impacts causing photo-chemical reactions, or by the internal influence of predissociation or internal conversion. Predissociation is not probable because the excitation took place mainly into the O,O band. The choice remains then between internal conversion and quenching through impacts, or perhaps by a combination of both effects. Internal conversion may

[29] J. Lecomte, J. de phys. et rad. 8, 489 (1937).

occur as a radiationless transition to the ground state or—more probably—to the lowest triplet state. According to measurements of Nauman[30] on the phosphorescence of substituted benzenes, this triplet state will be about 10,000 $cm^{-1}$ below the lowest singlet state in chlorobenzene. McClure[31] has observed that the lifetime of the lowest triplet state in chlorobenzene is $4 \cdot 10^{-3}$ sec.; hence the transition probability for the triplet-singlet intercombination is only about $10^3$ times smaller than for the lowest singlet-singlet transition. McClure pointed out that this results from the relatively strong spin-orbit interaction connected with the substitution of the heavy chlorine atom into the benzene ring. Kasha** consequently concluded that also the radiationless transition from the lowest excited singlet state to the triplet state should have a much higher probability when heavy substituents are involved.†† It is therefore quite possible that it is this radiationless singlet-triplet transition which is responsible for the non-occurrence of the fluorescence. However, since neither we nor Schüler and Woeldike[21,22] observed a light emission even in the spectral region of the phosphorescence, we must conclude that, even if the triplet state should become populated in the described fashion, its emission must be quenched by impacts. In this case, excitation energy may be used for photo-chemical processes. One may argue that the triplet state undergoes 1000 times more collisions during its lifetime than the excited singlet state, but the latter has a greater excitation energy and correspondingly greater sensitivity to quenching impacts. We believe that probably both radiationless transition and quenching impacts will be responsible for the non-occurrence of fluorescence and phosphorescence in the gaseous state. It is not possible at this time to make an estimate of the relative contributions of the processes to the quenching of the discussed emissions.

[30] R. V. Nauman, Ph.D. thesis, University of California (1947).
[31] D. S. McClure, J. Chem. Phys. **17**, 905 (1949).
** M. Kasha, discussion remark at Washington meeting of the American Physical Society (April, 1949).
†† It should be mentioned in this connection that Schüler (reference 22) also concluded, although on a different basis, that absence of ultraviolet light emission was connected with the mass of the substituent atom or group.

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# Spectra-Structure Correlations in the Infra-Red Region

N. B. COLTHUP
*Stamford Research Laboratories, American Cyanamid Company, Stamford, Connecticut*
(Received March 17, 1950)

This paper presents a chart giving probable positions of characteristic infra-red absorption bands for certain molecular groupings. Both original and published data were used in its preparation. The reliability of the various correlations is discussed in the text.

A CHART is presented summarizing our knowledge concerning the probable positions of the characteristic infra-red absorption bands of specific groups from 4000 to 400 wave numbers. Especial attention has been given to the region below 1400 wave numbers where specific group vibrations are complicated by their interaction with the rest of the molecule. This difficulty is particularly noticeable for assignments in the single bond region for such groups as ethyl, propyl, aldehyde, ketone, etc., where the bands are relatively weak and quite sensitive to the manner in which these groups are attached to the rest of the molecule.

Some of the data were taken from the literature and most of these have been rechecked and extended in the course of routine work. The rest of the correlations are made from unpublished work done in these Laboratories.

As some of the correlations are tentative and much overlapping of band positions occurs, this chart should be used with discretion mainly as an aid in extrapolating from known compounds to unknown samples.

The indicated regions on the chart are the regions within which the band is normally expected to fall. The abbreviations s, m, and w under the region markers indicate that the band is generally strong, medium, or weak.

The alkane groups are characterized by the well known carbon-hydrogen stretching (3000–2800 $cm^{-1}$)[1,2] and carbon-hydrogen bending (1475–1300 $cm^{-1}$)[1] bands. When the methyl group is attached to a nitrogen atom the 2900 $cm^{-1}$ bands generally shift to higher wave numbers and when it is on an oxygen atom the bands are lower. When the methyl is adjacent to a carbonyl as in acetates and methyl ketones, all the bands are shifted somewhat and the 1370 $cm^{-1}$ band is intensified. A similar intensification occurs for the 1420 $cm^{-1}$ band when a methylene is adjacent to a carbonyl or nitrile group. The C—H bending band at 1340 $cm^{-1}$ is weak in hydrocarbons but is intensified when this group is adjacent to an oxygen or nitrogen atom.

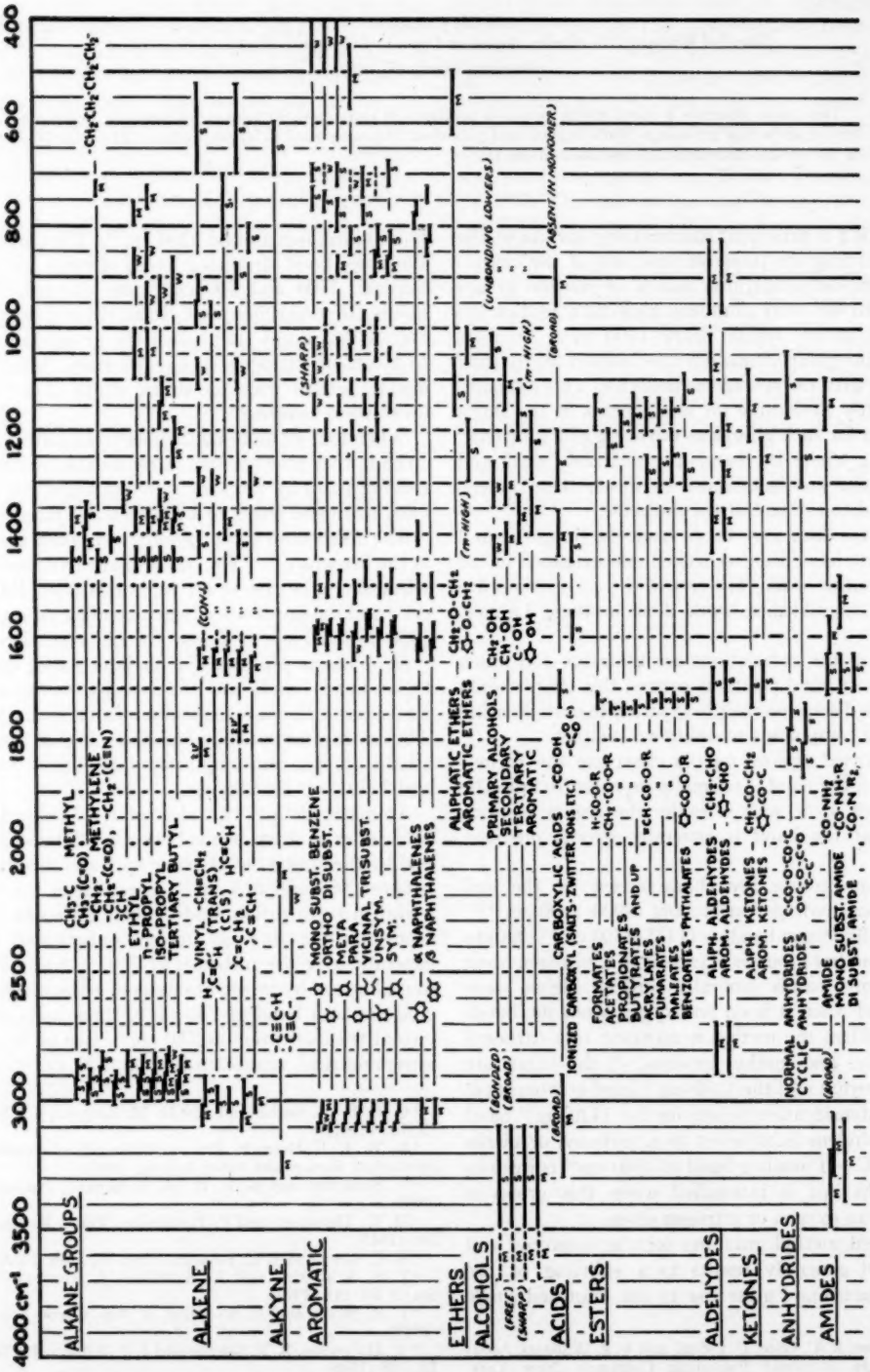
A branched methyl grouping such as isopropyl and tertiarybutyl generally results in a splitting of the 1370 $cm^{-1}$ band[1] and gives rise to the branched single bond vibrations around 1200 $cm^{-1}$.[3] The correlations of the single bond stretching bands of ethyl and *n*-propyl[4] between 1100 and 800 $cm^{-1}$ are less reliable as the bands are sometimes weak. In addition these particular correlations apply only when the groups are attached to a carbon, nitrogen, or oxygen atom. Attachment to heavier atoms such as sulfur shifts these bands to lower wave numbers.

When four or more methylene groups are adjacent in a chain, they give rise to a fairly reliable medium strong rocking band at 730 $cm^{-1}$.[5] When there are less than four, this band shifts to a higher wave number.

The alkene and alkyne groups have been well covered in the literature.[6–10] The out-of-plane hydrogen bending vibrations give rise to strong bands from 1000 to 600 $cm^{-1}$ and the in-plane hydrogen bending vibrations from 1450 to 1250 $cm^{-1}$. These are quite sensitive to the type of alkene present. The medium strong double and triple bond bands are lowered by conjugation and weakened if they are centrally located in the molecule. The hydrogen stretching bands are higher than for the alkane groups, centering around 3000 $cm^{-1}$ for alkenes and 3250 $cm^{-1}$ for alkynes.

Aromatic groups[1,11] are characterized below 1400 $cm^{-1}$ by a series of sharp bands between 1200 and 1000 $cm^{-1}$ and by the strong out-of-plane hydrogen bending bands between 900 and 675 $cm^{-1}$. These latter are the most useful in substitution studies. Five adjacent hydrogen atoms on the ring, as in monosubstituted benzene, generally give rise to bands at 700 $cm^{-1}$ and 740 $cm^{-1}$, four adjacent hydrogen atoms as in ortho disubstitution give rise to a band at 750 $cm^{-1}$, three as in meta and vicinal trisubstitution at 780 $cm^{-1}$, two as in para and unsymmetrical trisubstitution at 820 $cm^{-1}$, and one

[1] R. B. Barnes, R. C. Gore, U. Liddel, and V. Z. Williams, *Infra-red Spectroscopy* (Reinhold Publishing Company, New York, 1944).
[2] E. L. Saier and N. D. Coggeshall, Anal. Chem. **20**, 812 (1948).
[3] G. B. B. M. Sutherland and D. M. Simpson, J. Chem. Phys. **15**, 153 (1947).
[4] K. W. F. Kohlrausch, *Ramanspektren* (Akademische Verlagsgesellschaft Becker and Erler, Leipzig, 1943).
[5] N. Sheppard and G. B. B. M. Sutherland, Nature **159**, 739 (1947).
[6] H. W. Thompson and P. Torkington, Trans. Faraday Soc. **61**, 246 (1945).
[7] R. C. Gore and J. L. Johnson, Phys. Rev. **68**, 283A (1945).
[8] J. E. Kilpatrick and K. S. Pitzer, J. Research Nat. Bur. Stand. **38**, 191 (1947).
[9] J. H. Wotiz and F. A. Miller, J. Am. Chem. Soc. **71**, 3441 (1949).
[10] F. Halverson, R. F. Stamm and J. J. Whalen, J. Chem. Phys. **16**, 808 (1948).
[11] G. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, New York, 1945).


4000 cm⁻¹ 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400
ALKANE GROUPS
METHYL
METHYLENE
ETHYL
n-PROPYL
ISO-PROPYL
TERTIARY BUTYL
ALKENE
VINYL
(TRANS)
(CIS)
(CONJ.)
ALKYNE
AROMATIC
MONO SUBST. BENZENE
ORTHO DISUBST.
META
PARA
VICINAL TRISUBST.
UNSYM.
SYM.
α NAPHTHALENES
β NAPHTHALENES
(SHARP)
ETHERS
ALIPHATIC ETHERS
AROMATIC ETHERS
(m-HIGH)
(UNBONDING LOWERS)
ALCOHOLS
(BONDED)
(FREE)
(SHARP)
(BROAD)
PRIMARY ALCOHOLS
SECONDARY
TERTIARY
AROMATIC
(m-HIGH)
(BROAD)
(ABSENT IN NONOMER)
ACIDS
(BROAD)
IONIZED CARBOXYL (SALTS-ZWITTER IONS ETC)
CARBOXYLIC ACIDS
ESTERS
FORMATES
ACETATES
PROPIONATES
BUTYRATES AND UP
ACRYLATES
FUMARATES
MALEATES
BENZOATES-PHTHALATES
ALDEHYDES
ALIPH. ALDEHYDES
AROM. ALDEHYDES
KETONES
ALIPH. KETONES
AROM. KETONES
ANHYDRIDES
NORMAL ANHYDRIDES
CYCLIC ANHYDRIDES
(BROAD)
AMIDES
AMIDE
MONO SUBST. AMIDE
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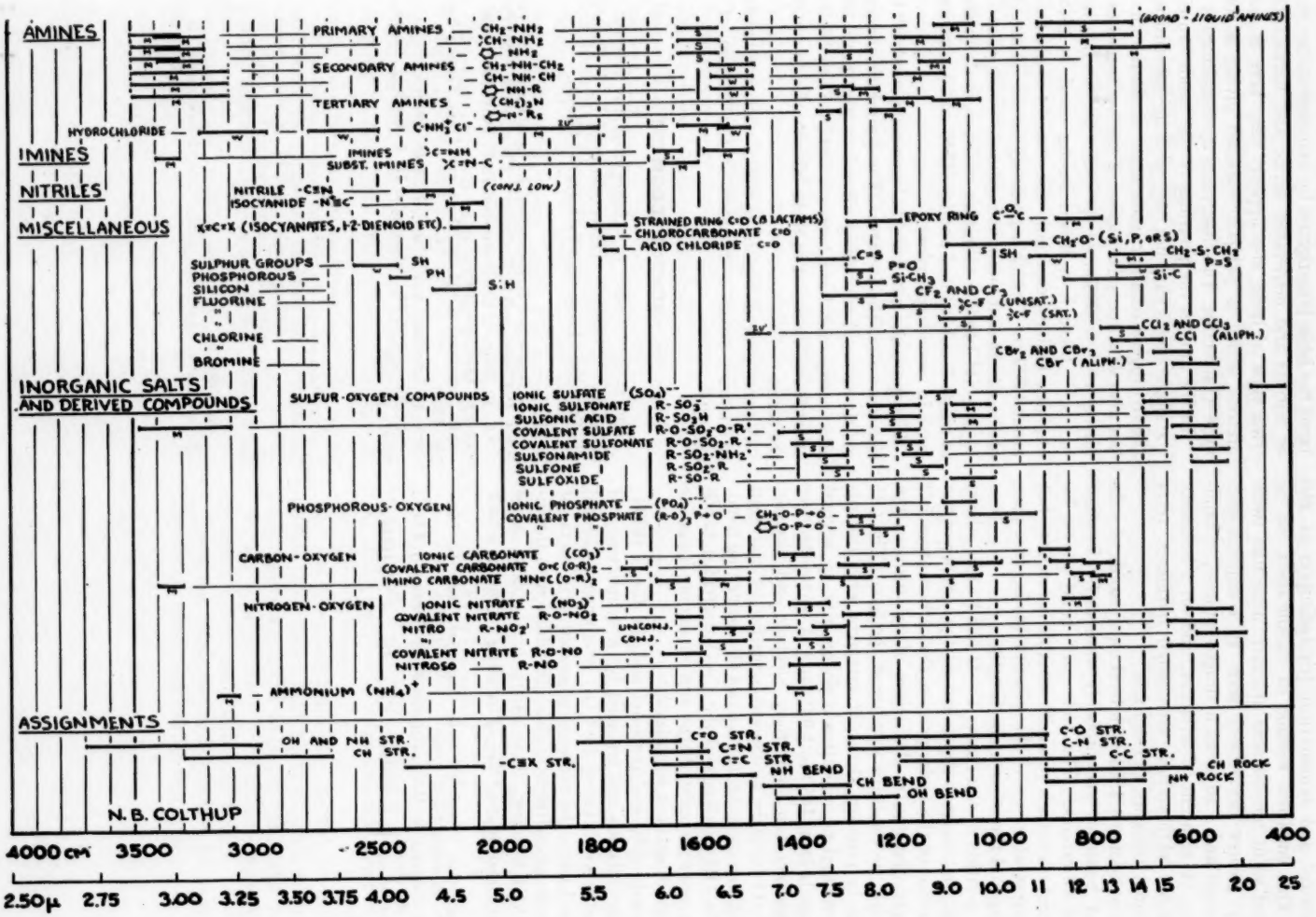


CHART 1. Probable positions of characteristic infra-red absorption bands.

isolated hydrogen atom on the ring as in meta, unsymmetrical and symmetrical trisubstitution at 860 $cm^{-1}$. This empirical method of classification can be extended to fit non-benzene aromatic molecules (with slightly greater deviations) such as $\alpha$-naphthalenes (4 adjacent and 3 adjacent hydrogen atoms), $\beta$-naphthalenes (4 adjacent, 2 adjacent, and on 1 isolated), substituted anthracenes, substituted pyridines, tetra substituted benzenes and steroids.

The well-known 1500 and 1600 $cm^{-1}$ bands of substituted benzenes are probably caused by in-plane skeletal vibrations.[11] The 1620 $cm^{-1}$ band shown by para disubstitution is generally variable in intensity but is strongest when one of the substituents is ortho-para directing and the other meta directing.

The position of the strong C—O band as in ethers, alcohols, and esters is dependent on the manner of the substitution of the hydrogens on the carbon atom.[12–14] Generally, the greater the degree of substitution, the higher will be the wave number of the band. The OH bending in primary alcohols[14] interacts with the adjacent methylene vibrations, giving rise to several weak bands from 1450 to 1300 $cm^{-1}$. A single stronger band appears here in tertiary alcohols and phenols. The C—O band in alcohols is sensitive to hydrogen bonding, just as is the well-known OH stretching band. Both the OH bending and the C—O stretching bands shift to lower wave numbers when unbonding occurs as it does on dilution or vaporization.

The carboxylic acid carbonyl and the C—O (1300–1200 $cm^{-1}$) bands are replaced by a symmetric and asymmetric vibration of the $CO_2^-$ group near 1420 and 1600 $cm^{-1}$ when the carboxyl is ionized as in metal or amine salts or zwitterionization. In addition to the in-plane COH bending, there exists, in the acid dimer only, an out-of-plane OH←O bending vibration which gives rise to a broad, medium band at 920 $cm^{-1}$. This band has been investigated by monomer-dimer studies of normal and deuterated acetic and formic acids.[15] This type of band also appears near here in acetylacetone which is partially enolized giving a similar OH←O structure. This disappears upon making the salt.

In the amines the positions of the bands caused by the single bonds vary not only with the substitution of the hydrogens on the carbon atom as do the alcohols but also with the substitution of the hydrogens on the nitrogen. In addition to the other well-known amine bands,[1,13] there is a broad strong band in primary aliphatic amines, especially the straight chain amines, around 800 $cm^{-1}$ which is probably caused by a rocking of the amino and methylene groups.[16,17] The band due to the NH bending vibration which is medium strong in mono N-substituted amides (1530 $cm^{-1}$) is generally weak in secondary amines.

The inorganic salts[11] and halogen compounds[11,18] have been covered in the literature. The symmetric and asymmetric sulfonyl stretching vibrations and those of related compounds have been studied by Schreiber[19] and others[20] and extended in these laboratories to complete the series.

A set of general regions in which various vibrational frequencies occur is included at the bottom of the chart.

ACKNOWLEDGMENT

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[12] J. Lecompte, Traité de Chimie Organique, Tome II (Masson et Cie, Éditeurs, Paris, 1936).
[13] V. Z. Williams, R. Hofstadter and R. C. Herman, J. Chem. Phys. **7**, 802 (1939).
[14] A. Borden and E. F. Barker, J. Chem. Phys. **6**, 553 (1938).
[15] L. G. Bonner and R. Hofstadter, J. Chem. Phys. **6**, 534 (1938).
[16] A. P. Cleaves and E. K. Plyler, J. Chem. Phys. **7**, 563 (1939).
[17] C. R. Baily, S. C. Carson, and E. F. Daly, Proc. Roy. Soc. (London) **A173**, 339 (1939).
[18] P. Torkington and H. W. Thompson, Trans. Faraday Soc. **41**, 236 (1945).
[19] V. C. Schreiber, Anal. Chem. **21**, 1168 (1949).
[20] D. Barnard, J. M. Fabian, and H. P. Koch, J. Chem. Soc. (1949), p. 2442.

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# Spectrophotometry in the Presence of Stray Radiation: A Table of Log$[(100-k)/(T-k)]$

ASCHER OFLER
*Research Department, Great Western Division, The Dow Chemical Company, Pittsburg, California*

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When spectrophotometry is conducted in the presence of unavoidable stray radiation, the usual expression for the absorbance $[A=\log(100/T)]$ becomes $\log[(100-k)/(T-k)]$, where $T$ is the percent transmittance $(100I/I_0)$ and $k$ is the percent stray radiation. To meet the demands of routine infra-red spectrophotometry in the 15–22$\mu$-region, a table of values of this function was prepared for $1<T<99$ and $0.5<k<20$. The calculation of these values was performed by punched card machines.

WHEN spectrophotometry must be performed in the presence of unavoidable stray radiation, it is necessary to eliminate or to correct for the false energy. This is especially important when long wave-lengths are used in infra-red spectrophotometry.

In the range above 15$\mu$, the unfavorable energy ratio between the desired wave-length and the wave-length of the blackbody maximum of the source causes rapid increases in the percent stray radiation with wave-length. This stray radiation may be virtually eliminated by the use of a double monochromator[1] or by judicious selection and use of reflection plates.[2] Most standard prism spectrometers provide some means of reducing the stray energy, e.g., rotating glass shutter, but the correction is never completely effective.

The extent of stray radiation may be estimated by two indirect methods:[3–5]

A. Measure the transmittance of a compound at various concentrations. Plot a family of curves using the formula $A=\log[(100-k)/(T-k)]$ for various $k$ (percent stray light) values. Select the curve which approaches nearest to a straight line. The corresponding $k$ is taken as the correct stray radiation.

B. The instrument is standardized at the desired wave-length and slit width. The radiation at the desired wave-length is absorbed while radiations of shorter wave-lengths, which are assumed to account for most of the stray radiation, are transmitted. This may be accomplished with a substance that absorbs strongly at that wave-length or with a filter of glass, mica, LiF, CaF, or NaCl.

In performing routine spectrophotometry in the 15–22$\mu$-range, stray radiation as high as 15 percent was encountered. As large numbers of measurements were made daily, considerable time was required for calculating suitable corrections. To simplify this operation, a table giving the corrected absorbance values for different stray energies was prepared. The 2251 values were computed by International Business Machines Company punched card machines.

The calculation was performed with an IBM No. 405 Tabulator equipped with card cycle total transfer device and an IBM No. 519 Reproducer serving as a summary punch. The equation $A=\log[(100-k)]/(T-k)]$ was transformed to $A=[\log(100-k)]-[\log(T-k)]$. The calculation was performed stepwise as follows:

A. 2500 Cards were prepared from 100 master "$T$" cards and 25 master "$k$" cards. Each card carried $T$, $k$, $(100-k)$, $\log(100-k)$, and $(2-\log T)$.

B. $(T-k)$ values were found by subtraction. Negative values were eliminated.

C. The logarithm values corresponding to the $(T-k)$ values were automatically selected and punched from a punched card table of logarithms.

D. The $[\log(T-k)]$ value was subtracted from the $[\log(100-k)]$ value.

E. The five-place table was checked by comparing random table values with individual calculations using a seven-place logarithm table. No errors were found.

F. The table was rounded off to four places by adding 5 to the last digit before dropping same.

The writer wishes to thank The Dow Chemical Company for permission to publish this table.

[1] Hawes, Cary, Beckman, Madsen, Hare, and Stickney, "A direct transmittancy recording infrared spectrophotometer," presented before the Symposium on Molecular Structure and Spectroscopy, June 17, 1949, at Columbus, Ohio.
[2] E. K. Plyler, J. Opt. Soc. Am. **37**, 746 (1947).
[3] Brattain, Rassmussen, and Cravath, J. App. Phys. **14**, 418 (1943).
[4] Fry, Nusbaum, and Randall, J. App. Phys. **17**, 158 (1946).
[5] J. R. Nielsen and Don C. Smith, Ind. Eng. Chem. *Anal. Ed.* **15**, 609 (1943).

TABLE I. Transmittance-absorbance conversion table for use in presence of stray radiation. $A = \log[(100-k)/(T-k)]$.

| $T$ | $K=0$ | 0.5 | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 | 6.0 | 7.0 | 8.0 | 9.0 | 10.0 | 11.0 | 12.0 | 13.0 | 14.0 | 16.0 | 18.0 | 20.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 99 | 0.0044 | 0.0044 | 0.0044 | 0.0044 | 0.0045 | 0.0045 | 0.0045 | 0.0045 | 0.0046 | 0.0046 | 0.0046 | 0.0047 | 0.0047 | 0.0048 | 0.0048 | 0.0049 | 0.0049 | 0.0050 | 0.0050 | 0.0051 | 0.0052 | 0.0053 | 0.0055 |
| 98 | 0.0088 | 0.0088 | 0.0089 | 0.0089 | 0.0090 | 0.0090 | 0.0091 | 0.0091 | 0.0091 | 0.0092 | 0.0092 | 0.0093 | 0.0094 | 0.0096 | 0.0097 | 0.0098 | 0.0099 | 0.0100 | 0.0101 | 0.0102 | 0.0105 | 0.0107 | 0.0110 |
| 97 | 0.0132 | 0.0133 | 0.0134 | 0.0134 | 0.0135 | 0.0136 | 0.0136 | 0.0137 | 0.0138 | 0.0139 | 0.0139 | 0.0141 | 0.0142 | 0.0144 | 0.0146 | 0.0147 | 0.0149 | 0.0151 | 0.0152 | 0.0154 | 0.0158 | 0.0162 | 0.0166 |
| 96 | 0.0177 | 0.0178 | 0.0179 | 0.0180 | 0.0181 | 0.0182 | 0.0183 | 0.0184 | 0.0185 | 0.0186 | 0.0187 | 0.0189 | 0.0191 | 0.0193 | 0.0195 | 0.0197 | 0.0200 | 0.0202 | 0.0204 | 0.0207 | 0.0212 | 0.0217 | 0.0223 |
| 95 | 0.0223 | 0.0224 | 0.0225 | 0.0226 | 0.0228 | 0.0229 | 0.0230 | 0.0231 | 0.0232 | 0.0234 | 0.0235 | 0.0237 | 0.0240 | 0.0243 | 0.0245 | 0.0248 | 0.0251 | 0.0254 | 0.0257 | 0.0260 | 0.0267 | 0.0273 | 0.0280 |
| 94 | 0.0269 | 0.0270 | 0.0272 | 0.0273 | 0.0274 | 0.0276 | 0.0277 | 0.0279 | 0.0280 | 0.0282 | 0.0283 | 0.0287 | 0.0290 | 0.0293 | 0.0296 | 0.0300 | 0.0303 | 0.0307 | 0.0310 | 0.0314 | 0.0322 | 0.0330 | 0.0339 |
| 93 | 0.0315 | 0.0317 | 0.0319 | 0.0320 | 0.0322 | 0.0324 | 0.0325 | 0.0327 | 0.0329 | 0.0331 | 0.0332 | 0.0336 | 0.0340 | 0.0344 | 0.0348 | 0.0352 | 0.0356 | 0.0360 | 0.0364 | 0.0369 | 0.0378 | 0.0388 | 0.0398 |
| 92 | 0.0362 | 0.0364 | 0.0366 | 0.0368 | 0.0370 | 0.0372 | 0.0374 | 0.0376 | 0.0378 | 0.0380 | 0.0382 | 0.0386 | 0.0391 | 0.0395 | 0.0400 | 0.0404 | 0.0409 | 0.0414 | 0.0419 | 0.0424 | 0.0435 | 0.0446 | 0.0458 |
| 91 | 0.0410 | 0.0412 | 0.0414 | 0.0416 | 0.0418 | 0.0421 | 0.0423 | 0.0425 | 0.0428 | 0.0430 | 0.0432 | 0.0437 | 0.0442 | 0.0447 | 0.0452 | 0.0458 | 0.0463 | 0.0469 | 0.0474 | 0.0480 | 0.0492 | 0.0505 | 0.0518 |
| 90 | 0.0458 | 0.0460 | 0.0463 | 0.0465 | 0.0468 | 0.0470 | 0.0473 | 0.0475 | 0.0478 | 0.0480 | 0.0483 | 0.0489 | 0.0494 | 0.0500 | 0.0506 | 0.0512 | 0.0518 | 0.0524 | 0.0530 | 0.0537 | 0.0551 | 0.0565 | 0.0580 |
| 89 | 0.0506 | 0.0509 | 0.0512 | 0.0514 | 0.0517 | 0.0520 | 0.0523 | 0.0526 | 0.0529 | 0.0531 | 0.0534 | 0.0541 | 0.0547 | 0.0553 | 0.0560 | 0.0566 | 0.0573 | 0.0580 | 0.0587 | 0.0594 | 0.0610 | 0.0626 | 0.0642 |
| 88 | 0.0555 | 0.0558 | 0.0561 | 0.0564 | 0.0567 | 0.0570 | 0.0574 | 0.0577 | 0.0580 | 0.0583 | 0.0586 | 0.0593 | 0.0600 | 0.0607 | 0.0614 | 0.0622 | 0.0629 | 0.0637 | 0.0645 | 0.0653 | 0.0670 | 0.0687 | 0.0706 |
| 87 | 0.0605 | 0.0608 | 0.0611 | 0.0615 | 0.0618 | 0.0621 | 0.0625 | 0.0628 | 0.0632 | 0.0636 | 0.0639 | 0.0646 | 0.0654 | 0.0662 | 0.0670 | 0.0678 | 0.0686 | 0.0694 | 0.0703 | 0.0712 | 0.0730 | 0.0750 | 0.0770 |
| 86 | 0.0655 | 0.0659 | 0.0662 | 0.0666 | 0.0670 | 0.0673 | 0.0677 | 0.0681 | 0.0685 | 0.0688 | 0.0692 | 0.0700 | 0.0709 | 0.0717 | 0.0726 | 0.0734 | 0.0743 | 0.0752 | 0.0762 | 0.0772 | 0.0792 | 0.0813 | 0.0836 |
| 85 | 0.0706 | 0.0710 | 0.0714 | 0.0718 | 0.0722 | 0.0726 | 0.0730 | 0.0734 | 0.0738 | 0.0742 | 0.0746 | 0.0755 | 0.0764 | 0.0773 | 0.0782 | 0.0792 | 0.0802 | 0.0812 | 0.0822 | 0.0832 | 0.0854 | 0.0877 | 0.0902 |
| 84 | 0.0757 | 0.0761 | 0.0766 | 0.0770 | 0.0774 | 0.0778 | 0.0783 | 0.0787 | 0.0792 | 0.0796 | 0.0801 | 0.0810 | 0.0820 | 0.0830 | 0.0840 | 0.0850 | 0.0861 | 0.0872 | 0.0883 | 0.0894 | 0.0918 | 0.0943 | 0.0969 |
| 83 | 0.0809 | 0.0814 | 0.0818 | 0.0823 | 0.0827 | 0.0832 | 0.0837 | 0.0842 | 0.0846 | 0.0851 | 0.0856 | 0.0866 | 0.0877 | 0.0887 | 0.0898 | 0.0909 | 0.0921 | 0.0932 | 0.0944 | 0.0957 | 0.0982 | 0.1009 | 0.1038 |
| 82 | 0.0862 | 0.0867 | 0.0872 | 0.0876 | 0.0881 | 0.0886 | 0.0891 | 0.0897 | 0.0902 | 0.0907 | 0.0912 | 0.0923 | 0.0934 | 0.0946 | 0.0957 | 0.0969 | 0.0981 | 0.0994 | 0.1007 | 0.1020 | 0.1047 | 0.1076 | 0.1107 |
| 81 | 0.0915 | 0.0920 | 0.0926 | 0.0931 | 0.0936 | 0.0941 | 0.0947 | 0.0952 | 0.0958 | 0.0963 | 0.0969 | 0.0981 | 0.0993 | 0.1005 | 0.1017 | 0.1030 | 0.1043 | 0.1056 | 0.1070 | 0.1084 | 0.1114 | 0.1145 | 0.1178 |
| 80 | 0.0969 | 0.0975 | 0.0980 | 0.0986 | 0.0991 | 0.0997 | 0.1003 | 0.1009 | 0.1015 | 0.1021 | 0.1027 | 0.1039 | 0.1052 | 0.1065 | 0.1078 | 0.1091 | 0.1105 | 0.1120 | 0.1135 | 0.1150 | 0.1181 | 0.1214 | 0.1249 |
| 79 | 0.1024 | 0.1030 | 0.1036 | 0.1041 | 0.1047 | 0.1053 | 0.1060 | 0.1066 | 0.1072 | 0.1078 | 0.1085 | 0.1098 | 0.1112 | 0.1125 | 0.1139 | 0.1154 | 0.1169 | 0.1184 | 0.1200 | 0.1216 | 0.1249 | 0.1285 | 0.1322 |
| 78 | 0.1079 | 0.1085 | 0.1092 | 0.1098 | 0.1104 | 0.1111 | 0.1117 | 0.1124 | 0.1130 | 0.1137 | 0.1144 | 0.1158 | 0.1172 | 0.1187 | 0.1202 | 0.1217 | 0.1233 | 0.1249 | 0.1266 | 0.1283 | 0.1319 | 0.1357 | 0.1397 |
| 77 | 0.1135 | 0.1142 | 0.1206 | 0.1155 | 0.1162 | 0.1168 | 0.1175 | 0.1182 | 0.1190 | 0.1197 | 0.1204 | 0.1219 | 0.1234 | 0.1249 | 0.1265 | 0.1282 | 0.1299 | 0.1316 | 0.1333 | 0.1352 | 0.1390 | 0.1430 | 0.1472 |
| 76 | 0.1192 | 0.1199 | 0.1206 | 0.1213 | 0.1220 | 0.1227 | 0.1235 | 0.1242 | 0.1249 | 0.1257 | 0.1265 | 0.1280 | 0.1296 | 0.1313 | 0.1330 | 0.1347 | 0.1365 | 0.1383 | 0.1402 | 0.1421 | 0.1461 | 0.1504 | 0.1549 |
| 75 | 0.1249 | 0.1257 | 0.1264 | 0.1272 | 0.1279 | 0.1287 | 0.1294 | 0.1302 | 0.1310 | 0.1318 | 0.1326 | 0.1343 | 0.1360 | 0.1377 | 0.1395 | 0.1413 | 0.1432 | 0.1451 | 0.1471 | 0.1492 | 0.1534 | 0.1579 | 0.1627 |
| 74 | 0.1308 | 0.1315 | 0.1323 | 0.1331 | 0.1339 | 0.1347 | 0.1355 | 0.1363 | 0.1372 | 0.1380 | 0.1389 | 0.1406 | 0.1424 | 0.1443 | 0.1461 | 0.1481 | 0.1501 | 0.1521 | 0.1542 | 0.1564 | 0.1609 | 0.1656 | 0.1707 |
| 73 | 0.1367 | 0.1375 | 0.1383 | 0.1391 | 0.1400 | 0.1408 | 0.1417 | 0.1426 | 0.1434 | 0.1443 | 0.1452 | 0.1471 | 0.1489 | 0.1509 | 0.1529 | 0.1549 | 0.1570 | 0.1592 | 0.1614 | 0.1637 | 0.1684 | 0.1735 | 0.1788 |
| 72 | 0.1427 | 0.1435 | 0.1444 | 0.1453 | 0.1461 | 0.1470 | 0.1479 | 0.1488 | 0.1498 | 0.1507 | 0.1517 | 0.1536 | 0.1556 | 0.1576 | 0.1597 | 0.1619 | 0.1641 | 0.1663 | 0.1687 | 0.1711 | 0.1761 | 0.1814 | 0.1871 |
| 71 | 0.1487 | 0.1496 | 0.1505 | 0.1515 | 0.1524 | 0.1533 | 0.1543 | 0.1552 | 0.1562 | 0.1572 | 0.1582 | 0.1602 | 0.1623 | 0.1645 | 0.1667 | 0.1689 | 0.1712 | 0.1736 | 0.1761 | 0.1786 | 0.1839 | 0.1895 | 0.1955 |
| 70 | 0.1549 | 0.1558 | 0.1568 | 0.1578 | 0.1587 | 0.1597 | 0.1607 | 0.1617 | 0.1627 | 0.1638 | 0.1648 | 0.1670 | 0.1691 | 0.1714 | 0.1737 | 0.1761 | 0.1785 | 0.1811 | 0.1837 | 0.1863 | 0.1919 | 0.1978 | 0.2041 |
| 69 | 0.1612 | 0.1621 | 0.1631 | 0.1641 | 0.1652 | 0.1662 | 0.1672 | 0.1683 | 0.1694 | 0.1704 | 0.1715 | 0.1738 | 0.1761 | 0.1785 | 0.1809 | 0.1834 | 0.1860 | 0.1886 | 0.1913 | 0.1941 | 0.2000 | 0.2062 | 0.2129 |
| 68 | 0.1675 | 0.1685 | 0.1696 | 0.1706 | 0.1717 | 0.1728 | 0.1739 | 0.1750 | 0.1761 | 0.1772 | 0.1784 | 0.1807 | 0.1832 | 0.1856 | 0.1882 | 0.1908 | 0.1935 | 0.1963 | 0.1992 | 0.2021 | 0.2083 | 0.2148 | 0.2219 |
| 67 | 0.1739 | 0.1750 | 0.1761 | 0.1772 | 0.1783 | 0.1794 | 0.1806 | 0.1818 | 0.1829 | 0.1841 | 0.1853 | 0.1878 | 0.1903 | 0.1929 | 0.1956 | 0.1984 | 0.2012 | 0.2041 | 0.2071 | 0.2102 | 0.2167 | 0.2236 | 0.2310 |
| 66 | 0.1805 | 0.1816 | 0.1827 | 0.1839 | 0.1851 | 0.1862 | 0.1874 | 0.1887 | 0.1899 | 0.1911 | 0.1924 | 0.1950 | 0.1976 | 0.2004 | 0.2032 | 0.2061 | 0.2090 | 0.2121 | 0.2152 | 0.2185 | 0.2253 | 0.2326 | 0.2403 |
| 65 | 0.1871 | 0.1883 | 0.1895 | 0.1907 | 0.1919 | 0.1931 | 0.1944 | 0.1957 | 0.1969 | 0.1982 | 0.1996 | 0.2023 | 0.2051 | 0.2079 | 0.2109 | 0.2139 | 0.2170 | 0.2202 | 0.2235 | 0.2269 | 0.2341 | 0.2417 | 0.2499 |
| 64 | 0.1938 | 0.1951 | 0.1963 | 0.1976 | 0.1988 | 0.2001 | 0.2014 | 0.2028 | 0.2041 | 0.2055 | 0.2069 | 0.2097 | 0.2126 | 0.2156 | 0.2187 | 0.2219 | 0.2251 | 0.2285 | 0.2320 | 0.2355 | 0.2430 | 0.2511 | 0.2596 |
| 63 | 0.2007 | 0.2019 | 0.2033 | 0.2046 | 0.2059 | 0.2072 | 0.2086 | 0.2100 | 0.2114 | 0.2128 | 0.2143 | 0.2173 | 0.2203 | 0.2234 | 0.2267 | 0.2300 | 0.2334 | 0.2369 | 0.2406 | 0.2443 | 0.2522 | 0.2606 | 0.2696 |
| 62 | 0.2076 | 0.2089 | 0.2103 | 0.2117 | 0.2131 | 0.2145 | 0.2159 | 0.2174 | 0.2188 | 0.2203 | 0.2219 | 0.2249 | 0.2281 | 0.2314 | 0.2348 | 0.2382 | 0.2418 | 0.2455 | 0.2493 | 0.2533 | 0.2615 | 0.2704 | 0.2798 |
| 61 | 0.2147 | 0.2161 | 0.2175 | 0.2189 | 0.2204 | 0.2218 | 0.2233 | 0.2249 | 0.2264 | 0.2280 | 0.2295 | 0.2328 | 0.2361 | 0.2395 | 0.2430 | 0.2467 | 0.2504 | 0.2543 | 0.2583 | 0.2624 | 0.2711 | 0.2803 | 0.2903 |
| 60 | 0.2219 | 0.2233 | 0.2248 | 0.2263 | 0.2278 | 0.2293 | 0.2309 | 0.2325 | 0.2341 | 0.2357 | 0.2374 | 0.2407 | 0.2442 | 0.2478 | 0.2515 | 0.2553 | 0.2592 | 0.2632 | 0.2674 | 0.2717 | 0.2808 | 0.2906 | 0.3010 |
| 59 | 0.2292 | 0.2307 | 0.2322 | 0.2338 | 0.2354 | 0.2370 | 0.2386 | 0.2402 | 0.2419 | 0.2436 | 0.2453 | 0.2489 | 0.2525 | 0.2562 | 0.2601 | 0.2640 | 0.2682 | 0.2724 | 0.2768 | 0.2813 | 0.2908 | 0.3010 | 0.3120 |
| 58 | 0.2366 | 0.2382 | 0.2398 | 0.2414 | 0.2430 | 0.2447 | 0.2464 | 0.2481 | 0.2499 | 0.2517 | 0.2534 | 0.2571 | 0.2609 | 0.2648 | 0.2688 | 0.2730 | 0.2773 | 0.2817 | 0.2863 | 0.2911 | 0.3010 | 0.3118 | 0.3233 |
| 57 | 0.2441 | 0.2458 | 0.2475 | 0.2492 | 0.2509 | 0.2526 | 0.2544 | 0.2562 | 0.2580 | 0.2598 | 0.2617 | 0.2656 | 0.2695 | 0.2736 | 0.2778 | 0.2821 | 0.2866 | 0.2913 | 0.2961 | 0.3010 | 0.3115 | 0.3228 | 0.3349 |
| 56 | 0.2518 | 0.2535 | 0.2553 | 0.2570 | 0.2588 | 0.2607 | 0.2625 | 0.2644 | 0.2663 | 0.2682 | 0.2702 | 0.2742 | 0.2783 | 0.2826 | 0.2869 | 0.2915 | 0.2962 | 0.3010 | 0.3061 | 0.3113 | 0.3222 | 0.3340 | 0.3468 |
| 55 | 0.2596 | 0.2614 | 0.2633 | 0.2651 | 0.2670 | 0.2688 | 0.2708 | 0.2727 | 0.2747 | 0.2767 | 0.2788 | 0.2829 | 0.2872 | 0.2917 | 0.2963 | 0.3010 | 0.3059 | 0.3110 | 0.3163 | 0.3217 | 0.3332 | 0.3456 | 0.3590 |
| 54 | 0.2676 | 0.2695 | 0.2714 | 0.2733 | 0.2752 | 0.2772 | 0.2792 | 0.2812 | 0.2833 | 0.2854 | 0.2875 | 0.2919 | 0.2964 | 0.3010 | 0.3058 | 0.3108 | 0.3159 | 0.3212 | 0.3267 | 0.3324 | 0.3445 | 0.3575 | 0.3716 |
| 53 | 0.2757 | 0.2777 | 0.2796 | 0.2816 | 0.2837 | 0.2857 | 0.2878 | 0.2899 | 0.2921 | 0.2943 | 0.2965 | 0.3010 | 0.3057 | 0.3106 | 0.3156 | 0.3208 | 0.3261 | 0.3317 | 0.3375 | 0.3434 | 0.3561 | 0.3697 | 0.3846 |

| | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 52 | 0.2840 | 0.2860 | 0.2881 | 0.2902 | 0.2923 | 0.2944 | 0.2966 | 0.2988 | 0.3010 | 0.3033 | 0.3056 | 0.3104 | 0.3153 | 0.3203 | 0.3256 | 0.3310 | 0.3366 | 0.3424 | 0.3485 | 0.3547 | 0.3680 | 0.3823 | 0.3979 |
| 51 | 0.2924 | 0.2945 | 0.2967 | 0.2988 | 0.3010 | 0.3033 | 0.3055 | 0.3078 | 0.3102 | 0.3126 | 0.3150 | 0.3199 | 0.3250 | 0.3303 | 0.3358 | 0.3415 | 0.3473 | 0.3534 | 0.3597 | 0.3663 | 0.3802 | 0.3953 | 0.4117 |
| 50 | 0.3010 | 0.3032 | 0.3054 | 0.3077 | 0.3100 | 0.3123 | 0.3147 | 0.3171 | 0.3195 | 0.3220 | 0.3245 | 0.3297 | 0.3350 | 0.3405 | 0.3463 | 0.3522 | 0.3583 | 0.3647 | 0.3713 | 0.3782 | 0.3928 | 0.4087 | 0.4260 |
| 49 | 0.3098 | 0.3121 | 0.3144 | 0.3168 | 0.3191 | 0.3216 | 0.3240 | 0.3265 | 0.3291 | 0.3316 | 0.3343 | 0.3397 | 0.3452 | 0.3510 | 0.3570 | 0.3632 | 0.3696 | 0.3763 | 0.3832 | 0.3904 | 0.4058 | 0.4225 | 0.4407 |
| 48 | 0.3188 | 0.3211 | 0.3235 | 0.3260 | 0.3285 | 0.3310 | 0.3336 | 0.3362 | 0.3388 | 0.3415 | 0.3443 | 0.3499 | 0.3557 | 0.3617 | 0.3680 | 0.3745 | 0.3812 | 0.3882 | 0.3955 | 0.4030 | 0.4191 | 0.4367 | 0.4559 |
| 47 | 0.3279 | 0.3304 | 0.3329 | 0.3354 | 0.3380 | 0.3406 | 0.3433 | 0.3460 | 0.3488 | 0.3516 | 0.3545 | 0.3604 | 0.3664 | 0.3727 | 0.3793 | 0.3860 | 0.3931 | 0.4004 | 0.4080 | 0.4160 | 0.4329 | 0.4514 | 0.4717 |
| 46 | 0.3372 | 0.3398 | 0.3424 | 0.3451 | 0.3478 | 0.3505 | 0.3533 | 0.3561 | 0.3590 | 0.3620 | 0.3649 | 0.3711 | 0.3774 | 0.3840 | 0.3908 | 0.3979 | 0.4053 | 0.4130 | 0.4210 | 0.4294 | 0.4472 | 0.4667 | 0.4881 |
| 45 | 0.3468 | 0.3495 | 0.3522 | 0.3550 | 0.3578 | 0.3606 | 0.3635 | 0.3665 | 0.3695 | 0.3725 | 0.3757 | 0.3821 | 0.3887 | 0.3956 | 0.4027 | 0.4102 | 0.4179 | 0.4260 | 0.4344 | 0.4431 | 0.4619 | 0.4825 | 0.5052 |
| 44 | 0.3566 | 0.3593 | 0.3622 | 0.3651 | 0.3680 | 0.3710 | 0.3740 | 0.3771 | 0.3802 | 0.3834 | 0.3867 | 0.3934 | 0.4003 | 0.4075 | 0.4150 | 0.4228 | 0.4309 | 0.4393 | 0.4482 | 0.4574 | 0.4771 | 0.4988 | 0.5229 |
| 43 | 0.3665 | 0.3694 | 0.3724 | 0.3754 | 0.3785 | 0.3815 | 0.3847 | 0.3879 | 0.3912 | 0.3945 | 0.3979 | 0.4049 | 0.4122 | 0.4197 | 0.4276 | 0.4357 | 0.4442 | 0.4531 | 0.4624 | 0.4721 | 0.4929 | 0.5159 | 0.5414 |
| 42 | 0.3768 | 0.3798 | 0.3829 | 0.3860 | 0.3892 | 0.3924 | 0.3957 | 0.3991 | 0.4025 | 0.4060 | 0.4095 | 0.4168 | 0.4244 | 0.4323 | 0.4405 | 0.4491 | 0.4580 | 0.4674 | 0.4771 | 0.4873 | 0.5093 | 0.5336 | 0.5607 |
| 41 | 0.3872 | 0.3904 | 0.3936 | 0.3968 | 0.4002 | 0.4035 | 0.4070 | 0.4105 | 0.4141 | 0.4177 | 0.4214 | 0.4291 | 0.4370 | 0.4453 | 0.4539 | 0.4629 | 0.4723 | 0.4821 | 0.4924 | 0.5031 | 0.5263 | 0.5521 | 0.5809 |
| 40 | 0.3979 | 0.4012 | 0.4046 | 0.4080 | 0.4115 | 0.4150 | 0.4186 | 0.4222 | 0.4260 | 0.4298 | 0.4337 | 0.4417 | 0.4500 | 0.4586 | 0.4677 | 0.4771 | 0.4870 | 0.4973 | 0.5082 | 0.5195 | 0.5441 | 0.5714 | 0.6021 |
| 39 | 0.4089 | 0.4124 | 0.4159 | 0.4194 | 0.4230 | 0.4267 | 0.4305 | 0.4343 | 0.4382 | 0.4422 | 0.4462 | 0.4546 | 0.4633 | 0.4724 | 0.4819 | 0.4918 | 0.5022 | 0.5131 | 0.5246 | 0.5366 | 0.5626 | 0.5916 | 0.6243 |
| 38 | 0.4202 | 0.4238 | 0.4274 | 0.4312 | 0.4349 | 0.4388 | 0.4427 | 0.4467 | 0.4508 | 0.4550 | 0.4592 | 0.4680 | 0.4771 | 0.4867 | 0.4966 | 0.5071 | 0.5180 | 0.5295 | 0.5416 | 0.5543 | 0.5819 | 0.6128 | 0.6478 |
| 37 | 0.4318 | 0.4355 | 0.4393 | 0.4432 | 0.4472 | 0.4512 | 0.4553 | 0.4595 | 0.4638 | 0.4681 | 0.4726 | 0.4818 | 0.4914 | 0.5014 | 0.5119 | 0.5229 | 0.5344 | 0.5465 | 0.5593 | 0.5728 | 0.6021 | 0.6351 | 0.6726 |
| 36 | 0.4437 | 0.4476 | 0.4516 | 0.4556 | 0.4598 | 0.4640 | 0.4683 | 0.4727 | 0.4771 | 0.4817 | 0.4864 | 0.4960 | 0.5061 | 0.5166 | 0.5277 | 0.5393 | 0.5515 | 0.5643 | 0.5778 | 0.5921 | 0.6233 | 0.6585 | 0.6990 |
| 35 | 0.4559 | 0.4600 | 0.4642 | 0.4684 | 0.4727 | 0.4771 | 0.4816 | 0.4862 | 0.4909 | 0.4957 | 0.5006 | 0.5107 | 0.5213 | 0.5324 | 0.5441 | 0.5563 | 0.5692 | 0.5828 | 0.5971 | 0.6123 | 0.6455 | 0.6834 | 0.7270 |
| 34 | 0.4685 | 0.4728 | 0.4771 | 0.4816 | 0.4861 | 0.4907 | 0.4954 | 0.5002 | 0.5052 | 0.5102 | 0.5153 | 0.5260 | 0.5371 | 0.5488 | 0.5611 | 0.5740 | 0.5877 | 0.6021 | 0.6173 | 0.6335 | 0.6690 | 0.7097 | 0.7570 |
| 33 | 0.4815 | 0.4859 | 0.4905 | 0.4951 | 0.4999 | 0.5047 | 0.5097 | 0.5147 | 0.5199 | 0.5252 | 0.5306 | 0.5418 | 0.5535 | 0.5659 | 0.5788 | 0.5925 | 0.6070 | 0.6223 | 0.6385 | 0.6558 | 0.6938 | 0.7377 | 0.7892 |
| 32 | 0.4949 | 0.4995 | 0.5043 | 0.5091 | 0.5141 | 0.5192 | 0.5244 | 0.5297 | 0.5351 | 0.5407 | 0.5464 | 0.5582 | 0.5705 | 0.5836 | 0.5973 | 0.6118 | 0.6272 | 0.6435 | 0.6608 | 0.6792 | 0.7202 | 0.7677 | 0.8239 |
| 31 | 0.5086 | 0.5135 | 0.5185 | 0.5236 | 0.5288 | 0.5342 | 0.5396 | 0.5452 | 0.5509 | 0.5568 | 0.5628 | 0.5752 | 0.5883 | 0.6021 | 0.6166 | 0.6320 | 0.6484 | 0.6657 | 0.6843 | 0.7041 | 0.7482 | 0.7999 | 0.8617 |
| 30 | 0.5229 | 0.5280 | 0.5332 | 0.5386 | 0.5441 | 0.5497 | 0.5554 | 0.5613 | 0.5673 | 0.5735 | 0.5798 | 0.5929 | 0.6068 | 0.6214 | 0.6368 | 0.6532 | 0.6706 | 0.6892 | 0.7091 | 0.7304 | 0.7782 | 0.8346 | 0.9031 |
| 29 | 0.5376 | 0.5430 | 0.5485 | 0.5541 | 0.5599 | 0.5658 | 0.5718 | 0.5780 | 0.5843 | 0.5908 | 0.5975 | 0.6114 | 0.6261 | 0.6416 | 0.6580 | 0.6755 | 0.6941 | 0.7140 | 0.7354 | 0.7584 | 0.8103 | 0.8724 | 0.9489 |
| 28 | 0.5528 | 0.5585 | 0.5643 | 0.5702 | 0.5763 | 0.5825 | 0.5888 | 0.5954 | 0.6021 | 0.6089 | 0.6160 | 0.6307 | 0.6463 | 0.6628 | 0.6803 | 0.6990 | 0.7189 | 0.7404 | 0.7634 | 0.7884 | 0.8451 | 0.9138 | 1.0000 |
| 27 | 0.5686 | 0.5746 | 0.5807 | 0.5869 | 0.5933 | 0.5998 | 0.6066 | 0.6135 | 0.6205 | 0.6278 | 0.6353 | 0.6509 | 0.6675 | 0.6850 | 0.7038 | 0.7238 | 0.7453 | 0.7684 | 0.7934 | 0.8206 | 0.8829 | 0.9596 | 1.0580 |
| 26 | 0.5850 | 0.5913 | 0.5977 | 0.6043 | 0.6110 | 0.6179 | 0.6250 | 0.6324 | 0.6399 | 0.6476 | 0.6555 | 0.6721 | 0.6897 | 0.7085 | 0.7286 | 0.7501 | 0.7733 | 0.7984 | 0.8256 | 0.8553 | 0.9243 | 1.0107 | 1.1249 |
| 25 | 0.6021 | 0.6087 | 0.6154 | 0.6224 | 0.6295 | 0.6368 | 0.6444 | 0.6521 | 0.6601 | 0.6683 | 0.6767 | 0.6944 | 0.7132 | 0.7333 | 0.7549 | 0.7782 | 0.8033 | 0.8305 | 0.8603 | 0.8931 | 0.9700 | 1.0687 | 1.2041 |
| 24 | 0.6198 | 0.6268 | 0.6339 | 0.6413 | 0.6488 | 0.6566 | 0.6646 | 0.6728 | 0.6812 | 0.6900 | 0.6990 | 0.7179 | 0.7380 | 0.7597 | 0.7830 | 0.8081 | 0.8355 | 0.8653 | 0.8981 | 0.9345 | 1.0212 | 1.1357 | 1.3010 |
| 23 | 0.6383 | 0.6456 | 0.6532 | 0.6610 | 0.6690 | 0.6773 | 0.6857 | 0.6945 | 0.7035 | 0.7128 | 0.7225 | 0.7427 | 0.7644 | 0.7877 | 0.8129 | 0.8403 | 0.8702 | 0.9031 | 0.9395 | 0.9803 | 1.0792 | 1.2148 | 1.4260 |
| 22 | 0.6576 | 0.6654 | 0.6734 | 0.6817 | 0.6902 | 0.6990 | 0.7080 | 0.7174 | 0.7270 | 0.7370 | 0.7473 | 0.7690 | 0.7924 | 0.8177 | 0.8451 | 0.8751 | 0.9080 | 0.9445 | 0.9853 | 1.0314 | 1.1461 | 1.3118 | 1.6021 |
| 21 | 0.6778 | 0.6861 | 0.6946 | 0.7034 | 0.7125 | 0.7218 | 0.7315 | 0.7415 | 0.7518 | 0.7625 | 0.7736 | 0.7970 | 0.8224 | 0.8499 | 0.8799 | 0.9129 | 0.9494 | 0.9902 | 1.0364 | 1.0894 | 1.2253 | 1.4367 | 1.9031 |
| 20 | 0.6990 | 0.7078 | 0.7169 | 0.7263 | 0.7360 | 0.7460 | 0.7563 | 0.7671 | 0.7782 | 0.7897 | 0.8016 | 0.8270 | 0.8545 | 0.8846 | 0.9177 | 0.9542 | 0.9952 | 1.0414 | 1.0944 | 1.1564 | 1.3222 | 1.6128 | |
| 19 | 0.7213 | 0.7307 | 0.7404 | 0.7504 | 0.7608 | 0.7715 | 0.7827 | 0.7942 | 0.8062 | 0.8186 | 0.8316 | 0.8592 | 0.8893 | 0.9224 | 0.9590 | 1.0000 | 1.0463 | 1.0994 | 1.1614 | 1.2355 | 1.4472 | 1.9138 | |
| 18 | 0.7447 | 0.7548 | 0.7652 | 0.7760 | 0.7871 | 0.7987 | 0.8107 | 0.8232 | 0.8361 | 0.8497 | 0.8638 | 0.8940 | 0.9271 | 0.9638 | 1.0048 | 1.0512 | 1.1043 | 1.1663 | 1.2406 | 1.3324 | 1.6233 | | |
| 17 | 0.7696 | 0.7803 | 0.7915 | 0.8031 | 0.8151 | 0.8276 | 0.8406 | 0.8542 | 0.8683 | 0.8831 | 0.8985 | 0.9317 | 0.9685 | 1.0096 | 1.0560 | 1.1091 | 1.1712 | 1.2455 | 1.3375 | 1.4574 | 1.9243 | | |
| 16 | 0.7959 | 0.8075 | 0.8196 | 0.8321 | 0.8451 | 0.8587 | 0.8728 | 0.8876 | 0.9031 | 0.9193 | 0.9363 | 0.9731 | 1.0142 | 1.0607 | 1.1139 | 1.1761 | 1.2504 | 1.3424 | 1.4624 | 1.6335 | | | |
| 15 | 0.8239 | 0.8365 | 0.8495 | 0.8631 | 0.8773 | 0.8921 | 0.9076 | 0.9238 | 0.9409 | 0.9588 | 0.9777 | 1.0189 | 1.0654 | 1.1187 | 1.1809 | 1.2553 | 1.3473 | 1.4674 | 1.6385 | 1.9345 | | | |
| 14 | 0.8570 | 0.8675 | 0.8817 | 0.8965 | 0.9121 | 0.9283 | 0.9454 | 0.9633 | 0.9823 | 1.0023 | 1.0235 | 1.0700 | 1.1234 | 1.1856 | 1.2601 | 1.3522 | 1.4723 | 1.6435 | 1.9395 | | | | |
| 13 | 0.8861 | 0.9009 | 0.9165 | 0.9327 | 0.9498 | 0.9678 | 0.9868 | 1.0068 | 1.0280 | 1.0506 | 1.0746 | 1.1280 | 1.1903 | 1.2648 | 1.3570 | 1.4771 | 1.6484 | 1.9445 | | | | | |
| 12 | 0.9208 | 0.9371 | 0.9543 | 0.9723 | 0.9912 | 1.0113 | 1.0325 | 1.0551 | 1.0792 | 1.1049 | 1.1326 | 1.1950 | 1.2695 | 1.3617 | 1.4819 | 1.6532 | 1.9494 | | | | | | |
| 11 | 0.9586 | 0.9766 | 0.9956 | 1.0157 | 1.0370 | 1.0596 | 1.0837 | 1.1095 | 1.1372 | 1.1671 | 1.1996 | 1.2742 | 1.3664 | 1.4867 | 1.6580 | 1.9542 | | | | | | | |
| 10 | 1.0000 | 1.0201 | 1.0414 | 1.0640 | 1.0881 | 1.1139 | 1.1417 | 1.1716 | 1.2041 | 1.2396 | 1.2788 | 1.3711 | 1.4914 | 1.6628 | 1.9590 | | | | | | | | |
| 9 | 1.0458 | 1.0684 | 1.0926 | 1.1184 | 1.1461 | 1.1761 | 1.2086 | 1.2442 | 1.2833 | 1.3268 | 1.3757 | 1.4960 | 1.6675 | 1.9638 | | | | | | | | | |
| 8 | 1.0969 | 1.1228 | 1.1505 | 1.1805 | 1.2131 | 1.2486 | 1.2878 | 1.3313 | 1.3802 | 1.4359 | 1.5006 | 1.6721 | 1.9685 | | | | | | | | | | |
| 7 | 1.1549 | 1.1849 | 1.2175 | 1.2531 | 1.2923 | 1.3358 | 1.3847 | 1.4405 | 1.5052 | 1.5821 | 1.6767 | 1.9731 | | | | | | | | | | | |
| 6 | 1.2219 | 1.2575 | 1.2967 | 1.3402 | 1.3892 | 1.4449 | 1.5097 | 1.5866 | 1.6812 | 1.8039 | 1.9777 | | | | | | | | | | | | |
| 5 | 1.3010 | 1.3446 | 1.3936 | 1.4494 | 1.5141 | 1.5911 | 1.6857 | 1.8084 | 1.9823 | | | | | | | | | | | | | | |
| 4 | 1.3979 | 1.4538 | 1.5185 | 1.5955 | 1.6902 | 1.8129 | 1.9868 | | | | | | | | | | | | | | | | |
| 3 | 1.5229 | 1.5999 | 1.6946 | 1.8174 | 1.9912 | | | | | | | | | | | | | | | | | | |
| 2 | 1.6990 | 1.8217 | 1.9956 | | | | | | | | | | | | | | | | | | | | |

# In Memoriam

## Archie G. Worthing

The Optical Society of America lost one of its distinguished members and a former president (1941–43) in the sudden death of Dr. Archie Garfield Worthing on July 30, 1949. He had been an outstanding scientist, particularly in the field of high temperature measurements and properties of tungsten, as well as a patient and thought-provoking teacher.

Dr. Worthing was born February 6, 1881 at LeRoy, Wisconsin, and received his A.B. degree from the University of Wisconsin in 1904 and Ph.D. from the University of Michigan in 1911. He had also taught at the University of Iowa during this interval. After working at the Nela Research Laboratories in Cleveland, Ohio, he went to the University of Pittsburgh where he was head of the Physics Department from 1925–37 and Professor of Physics until his death.

His contributions to scientific journals were very numerous. Alone or with others he published over 40 papers, many of them in the fields of high temperature measurements and in the teaching of physics. He also authored or co-authored four books, including: *An Outline of Atomic Physics* (with other staff members of the Physics Department at the Univeristy of Pittsburgh), *Treatment of Experimental Data* (with Joseph Geffner), *Heat* (with David Halliday), and *Measurements of Radiant Energy* (edited by W. E. Forsythe). He was a Fellow of The American Physical Society and a member and past president of both the Optical Society of America and the American Association of Physics Teachers. He was on the governing board of the American Institute of Physics. He was also a conscientious worker on a number of other national committees in the fields of physics and the teaching of this subject. His honor fraternities included Phi Beta Kappa, Sigma Xi, and Sigma Pi Sigma. He was faculty adviser for the latter group at the University of Pittsburgh.

Dr. Worthing's teaching career was unique both on the undergraduate and the graduate level. In his well-named course, Basic Concepts in Physics, exact definitions and nomenclature were stressed, as much as the basic ideas behind formulas. His course in Heat was highly original and thorough. In his dealings with students, he was outstandingly fair and patient. He encouraged them to think for themselves.

In memory of Dr. Worthing's work in science and his deep interest in students, there has been established in the Physics Department of the University of Pittsburgh a Worthing Memorial Fund. This is being financed by contributions from his former students and friends. It will honor each year, starting in 1950, one senior student who has done outstanding work during his undergraduate days and who shows great promise in the field of physics. The award carries a prize of one hundred dollars.

The sympathies of all members of the Optical Society of America are extended to Dr. Worthing's family.

MARY E. WARGA
L. O. GRONDAHL

ARCHIE G. WORTHING

## Perley G. Nutting

It seems fitting that the Optical Society of America should take respectful notice of the death of its founder Perley G. Nutting on August 8, 1949. Perley Gilman Nutting must be recognized as the man who conceived the idea of the Optical Society of America and who acted to implement its organization. I had the great good fortune to be closely associated with Dr. Nutting during those years when he was actively engaged in laying the foundation upon which the edifice of the Optical Society was later erected. During the years 1910 to 1912, while he and I worked together at the National Bureau of Standards, I had frequent occasions to hear his expressions of opinion that a national society for all scientists and technologists interested particularly in the field of optics would be very desirable. As far as I am aware, however, no actual steps were taken toward the formation of such an organization until after he came to Rochester, in the latter part of 1912, as assistant director of the Kodak Research Laboratories and as head of the physics department.

Rochester, New York, seemed a particularly suitable location in which the initial steps toward the realization of his dream could be taken. On November 18, 1915, Dr. Nutting invited a group of about fifteen interested people to meet with him to discuss plans for the formation of a group in Rochester under the name of "Society for the Advancement of Applied Optics." The suggestion met with the enthusiastic approval of most of those present and Dr. Nutting proceeded to draft the Constitution and By-Laws. On December 17, 1915, a second meeting was held at which the proposed Constitution and By-Laws were discussed and, after minor revisions, were signed by fourteen charter members. Dr. Nutting was elected the first president of this society.

Prior to and following the organization of the Rochester group, Dr. Nutting had been in communication by mail with many leaders in the field of optics throughout the United States proposing the formation of a national society. The response received seemed favorable and, on December 28, 1916, the first meeting was held under the auspices of the American Association for the Advancement of Science. Dr. Nutting was elected the first president of the national organization and served during the years 1916–1917. At this first meeting Dr. Nutting read two papers, one "A Photochemical Theory of Vision and Photographic Action," and another "A Proposed New Method of Classification for Optical Glass." The first of these was published in the *Journal of the Optical Society of America* **1**, 31 (1917).

When the national society was organized, the name "Optical Society of America" was adopted and the Rochester group changed the name of their organization to the "Rochester Section of the Optical Society of America."

It is clear from what has been said above that there is little doubt that Dr. Nutting was the leader and the moving spirit in the formation of the Optical Society of America. I feel that the members of the Optical Society should pay tribute to his memory

PERLEY G. NUTTING

by recognizing the signal service which he performed in the launching of our organization.

Dr. Nutting was a prolific writer and published nearly two hundred scientific communications and reports in various technical journals. In addition to being a research physicist of the first order and an able director of research, he possessed those personal qualities which endeared him to all those with whom he was associated. He was generous, kindly, and considerate, and especially concerned with the welfare and happiness of those who worked under his direction. Those who knew him intimately mourn his passing and feel poignantly a personal loss.

Dr. Nutting was born in Randolph, Wisconsin, August 22, 1873. He took his B.A. degree at Leland Stanford in 1897 and his M.S. degree at the University of California in 1899. Following this he went to Germany as Whiting Fellow and studied optics at Göttingen during 1901 and 1902. After returning to this country he obtained the degree of Ph.D. from Cornell University in 1903. He then went to the Bureau of Standards as assistant physicist and in 1909 became associate physicist in charge of the optics section of the Bureau of Standards. He remained in this position until the latter part of 1912, at which time he accepted the position as assistant director of the Kodak Research Laboratories which had just been organized under the direction of Dr. C. E. K. Mees. Dr. Nutting remained in the Kodak Laboratories until the latter part of 1916 when he accepted the position as director of research for the Westinghouse Electric and Manufacturing Company in Pittsburgh, holding this position until 1920. From 1920 to 1925 he was active as a consultant engineer on various optical projects, among which may be mentioned the illumination of stage sets for the making of color motion pictures in association with Maude Adams. Dr. Nutting designed the first of the large incandescent lamps (from 10 to 100 kilowatts) which are mentioned in his article in J. Opt. Soc. Am. **7**, 402 (1923). The patents on these lamps were later taken over by the General Electric Company. In 1925 he became associated with the Geological Survey in Washington, D. C., as a geophysicist, remaining in this position until his retirement in 1943.

Dr. Nutting was a member of the American Association for the Advancement of Science, Physical Society, Astronomical Society, Optical Society of America (President, 1917), American Chemical Society, and the Washington Academy of Science. During the years spent in obtaining his university training and in the subsequent years spent at the Bureau of Standards and in the Kodak Research Laboratories he was interested chiefly in the many phases of the science of optics and published numerous papers in this field. After the first world war, he turned his attention to physical chemistry and geophysics, and continued in these fields until his death.

In 1906 he married Edith Eva Lightfoot. After her death he married Julia E. Stouffer in 1928. He is survived by his wife and four sons, Ian F. Nutting of Pittsburgh, Navy Captain Kelvin L. Nutting of the Great Lakes Naval Training Center, Edward V. Nutting, and Perley G. Nutting, Jr. of Washington, D. C.

LOYD A. JONES

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## Course in Modern Industrial Spectrography at Boston College

Boston College has announced a special two weeks intensive course in Modern Industrial Spectrography at Chestnut Hill, Boston, Massachusetts, from July 24 to August 4. The course is particularly designed for chemists and physicists from industries in the process of installing spectrographic equipment. Information on the course can be obtained from Professor James J. Devlin, Physics Department, Boston College, Chestnut Hill, Boston 67, Massachusetts.

# Book Reviews

**Luminescent Materials.** G. F. J. GARLICK. Pp. 254. Oxford University Press, London, 1949. Price $5.50.

Among the several texts on luminescence that have been published during the past year, this book is the smallest and most readable. Obviously, it is not the most comprehensive.

The subject matter primarily concerns the properties of inorganic luminescent solids with ultraviolet excitation and the interpretations of these properties. Infra-red stimulation and quenching are also discussed. The electrical properties of phosphors are presented in considerable detail. There is also a chapter on cathodoluminescence and one on organic phosphors. Naturally, the author strongly emphasizes his own research and the research of his predecessors, Randall and Wilkins, at the University of Birmingham. The presentation is at a fundamental level, but is quite non-mathematical. Considerable speculation is apparent. Often Garlick deduces detailed conclusions from qualitative exploratory data, for example, thermoluminescence data obtained at inordinately fast heating rates and presented with no indication of probable error. His interpretations are frequently at variance with the published research of other investigators. Innumerable experiments—some significant, many obvious—are proposed. Technical applications are not included.

The reviewer is on record as being in complete accord with the philosophy of the author quoted as follows from the final paragraph of the text: ". . . Future improvements of phosphors for practical purposes will depend less upon empirical methods of investigation and more upon the attention given to the fundamental mechanisms of luminescence. . . ."The reviewer recommends this book as a valuable text for investigators active in the field of solid-state luminescence.

FERD E. WILLIAMS
*Research Laboratory*
*General Electric Company*
*Schenectady, New York*

**An Introduction to Luminescence of Solids.** HUMBOLDT W. LEVERENZ. Pp. 569+xv. John Wiley and Sons, Inc., New York, 1950. Price $12.00.

A concise summary of our present-day concept of atomic and molecular structure and properties concerned with electron shells, valence binding forces, and molecular states is laid down as the groundwork for the reader and as an aid to better appreciation of the principal subject. There follows a broad discussion of crystal states and then the major phases of phosphor synthesis, constitution, mechanism, characteristic properties and uses.

Primary emphasis is placed on the inorganic types of phosphor or luminescent solid and in particular on the synthetic production and applications. One is impressed by the analytical precision and minute quantities which are involved. The author indicates that spectroscopic purity may in general be considered as about 99.999 percent whereas luminescent effects are such as to involve another decimal place with 99.9999 percent being considered as luminescence pure; and yet it is the minute amount of impurity to which most of the nonstoichiometric combinations owe their luminescent properties. Directions are included for the preparation of representative phosphors and an appendix provides information on methods of obtaining purified principal constituents.

Dr. Leverenz has provided a thorough presentation of the theory of phosphor absorption and emission of radiant energy. The section on application is particularly well developed and seems to complete an exceptionally well-developed reference work. Extensive appendices are supplied in specialized topics together with definitions of terms and symbols. A unique periodic table of elements and their properties is provided for reader reference. Literature citations are collected by chapters which may be confusing but this difficulty is partially offset by a unique and useful index of inorganic materials by formulas.

WALLACE R. BRODE
*National Bureau of Standards*
*Washington, D. C.*

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# Letters to the Editor

## Comments on "The Design of Triplet Anastigmat Lenses of the Taylor Type"

WARREN J. SMITH
*Simpson Optical Manufacturing Company, Chicago, Illinois*
March 9, 1950

IN R. E. Stephens' article "Design of triplet anastigmat lenses of the Taylor type,"[1] there is an omission in the expansion of the determinant on p. 1036 into Eq. (26). Equation (26) lacks the term $A$, which represents the power of the system, and as it stands will yield incorrect solutions for $h_2$, the ray height at the second lens of the triplet. The error is a rather insidious one since Eq. (26) as published will give a reasonable value of $h_2$, and the complete solution of the triplet will satisfy all of the desired conditions except a zero value for lateral color. Obviously if the selected value of $A$ should be unity, Eq. (26) is correct. The complete expansion of the determinant is as follows:

Corrected Eq. (26):

$$\begin{aligned}O=&h_2^2[Am_1\mu_2\mu_3h_3-Am_3\mu_1\mu_2+P\mu_2h_3(\mu_1-\mu_3)]\\&+h_2^2[Am_2\mu_1(\mu_1+\mu_2)-Am_1\mu_3h_3^2(\mu_1+\mu_2)\\&-P\mu_1h_3(\mu_1+\mu_3-\mu_3)+P\mu_2\mu_3h_3^2\\&+Qm_1h_3(\mu_1-\mu_3)]\\&+h_2[A\mu_1\mu_3h_3^2(m_1+m_2)-Am_2\mu_1\mu_3h_3\\&-Am_3\mu_1^2+P\mu_1h_3(\mu_1-\mu_3h_3)\\&+Qh_3(m_2\mu_3-m_3\mu_1-m_1\mu_1+m_1\mu_3h_3)]\\&+[Qm_2h_3(\mu_1-\mu_3h_3)].\end{aligned}$$

In like manner, expanding the determinant with $Q$ equal to zero: Corrected Eq. (27):

$$\begin{aligned}O=&h_2^2[Ph_3\mu_2(\mu_1-\mu_2)+Am_1h_3\mu_2\mu_3-Am_3\mu_1\mu_2]\\&+h_2[Am_2\mu_1(\mu_1+\mu_2)-Am_1h_3^2\mu_3(\mu_1+\mu_2)\\&-\mu_1Ph_3(\mu_1+\mu_3-\mu_3)+\mu_2\mu_3Ph_3^2]\\&+[A\mu_1\mu_3h_3^2(m_1+m_2)-Am_2\mu_1\mu_3h_3\\&-Am_3\mu_1^2+\mu_1Ph_3(\mu_1-\mu_3h_3)].\end{aligned}$$

Stephens' methods of triplet design are pleasantly straightforeward and utilize all the variables subject to convenient third-

order manipulation; as such they should greatly encourage many confronted by the winding paths of optical design.

[1] R. E. Stephens, J. Opt. Soc. Am. **38**, 1032 (1948).

ROBERT E. STEPHENS
*National Bureau of Standards, Washington, D. C.*
March 23, 1950

I CONCUR with W. J. Smith's corrections of Eqs. (26) and (27) in my paper "The design of triplet anastigmat lenses of the Taylor type." The omission of "$A$" from those equations is serious unless $A=1$ (the usual choice).

Some other errors in this paper of less serious nature have been found. While these probably do not cause a reader much difficulty, perhaps they should be pointed out. All the $h$'s appearing before Eqs. (5) on p. 1032 should be bold face, representing heights of incidence, with the dimension length. On p. 1035, line 5, $h_3$ should be bold face. In line 6, $\left(\frac{h_1}{h_3}\right)$ should be squared.

## The Emission Bands of Willemite in Phosphorescence

ELEMÉR NAGY
*Research Laboratory, United Incandescent Lamp and Electrical Company, Ujpest, Budapest, Hungary*
January 3, 1950

IT has been established by Szigeti and Nagy[1,2] and confirmed by Butler[3] and Shrader[4] that the fluorescence emission spectrum of zinc silicate activated by manganese can be resolved into at least four bands. These bands were found at 2.48, 2.35, 2.27, 2.17, and 2.05 ev. They were little affected by temperature changes, but showed a steady shift toward longer wave-lengths on increasing the manganese concentration.

The phosphorescence of zinc silicates by cathode-ray excitation of varying duration from 1 μsec. up to 10 msec. was measured by Gergely.[5] He has found that the decay is exponential with a time constant of 5–15 msec. only, when the excitation time is above a millisecond. By using shorter excitation, more rapid processes begin to be seen with decay constants of approximately 2000 and 70,000. These new processes seem also to have a monomolecular character. The entire decay can be analyzed into a superposition of three single exponential decays. The rapid processes are more and more preponderant as the excitation time is shortened.

Measurements were made, therefore, to investigate whether the phosphorescence characterized by these various time constants represent the same emission spectrum, or whether they belong to distinct subbands. The phosphorescence emission spectrum of the willemite was determined by painting a revolving disk uniformly with the fluorescent powder and by projecting the phosphorescent light after 2–5 msec. through a little hole to the spectrograph slit. The measurements could be reproduced well within two percent on three separate runs. In Fig. 1 the emission spectrum is exhibited for the fluorescence at equilibrium and for the phosphorescence after 3 msec.

The phosphorescent spectrum is entirely symmetrical if plotted in photon numbers *vs.* energy, and the disappearance of the

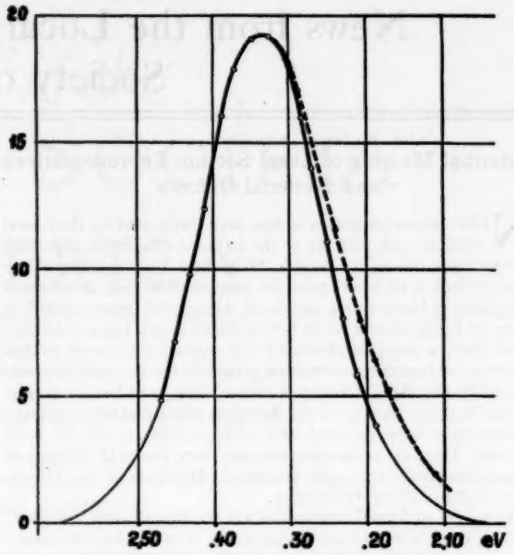


FIG. 1. Fluorescent and phosphorescent emission spectra of willemite drawn to the same scale. Fluorescence denoted with dots, phosphorescence with open circles. The blue sides coincide.

yellow subbands is established beyond doubt. This new experimental evidence proves that the separation of the fluorescence emission spectrum into components has a sound basis. The latter bands are symmetrical and have almost exactly the shape of Gaussian error curves if plotted in photon numbers *vs.* energy. The symmetrical main band at 2.35 ev was found to have the well-known decay constant of 70–200 sec.$^{-1}$. The subbands have higher decay constants, for these have completely disappeared after a phosphorescence of 3 msec.

Similar observations were made on the apparatus used by Dr. Gergely[5] in his phosphorescence measurements. By interposing suitable light filters between the fluorescent spot on the cathode-ray tube and the multiplier cathode, the relative amplitude of the short and slow phosphorescence processes could be varied in wide ranges.

It was found, for example, that the shortest process ($\alpha=70{,}000$) is that luminescing in a blue or bluish green color. A green filter removes almost everything except the slow phosphorescence. A yellow filter completely removes the very short process, diminishes the green one (2.35 ev) and steepens the decay of phosphorescence, a phenomenon which may be interpreted as due to a greater preponderance of the yellow bands.

It is therefore very probable that the very short process in the willemite phosphorescence is blue or bluish green, that the exponential decay of 5–15 msec. corresponds to the main band only 2.35 ev, and that the yellow subbands have a decay constant of approximately 2000.

Detailed data will be published soon.

[1] Szigeti and Nagy, Müegyetemi Közlemények (1948).
[2] E. Nagy, J. Opt. Soc. Am. **39**, 42 (1949).
[3] K. H. Butler, J. Electrochem. Soc. **93**, 143 (1948).
[4] R. E. Shrader, J. Opt. Soc. Am. **39**, 699 (1949).
[5] G. Gergely, J. Opt. Soc. Am. **40**, 357 (1950).

# News from the Local Sections of the Optical Society of America

## Informal Meeting of Local Section Representatives and National Officers

NINE representatives who had been designated by their local sections met with six of the national officers for breakfast one morning during the March, 1950, New York meeting of the Optical Society of America for the purpose of holding an informal discussion of local section problems. Among the items considered were the Local Section News Letter, which is now being published three times a year; the desirability of running some local section news in the Journal; and meeting programs for the local sections, especially the visiting lecturers whose trips have been arranged by the National Society for the last three years, and whose presentations have been received with such enthusiasm by the local sections. This year's traveling lecturers were Bruce H. Billings of Baird Associates, Inc., and George R. Harrison of the Massachusetts Institute of Technology.

Although no formal conclusions are reached at such meetings, nor are definite recommendations made, it is felt by all persons concerned that these semi-annual get-togethers provide an excellent opportunity for representatives of the various local sections to discuss with each other their problems of mutual interest and to suggest possible methods of solution for some of them. Also, this provides a convenient mechanism for keeping the national officers alerted to the special problems arising in our fast growing local section program. The next such get-together will be scheduled for the Cleveland meeting of October 26–28, 1950.

## Installation of the Chicago Section of the Optical Society of America

THE sixth local section of the Optical Society of America came into existence on May 24, 1950, when the Optical Society of Chicago was formally installed as our Chicago Section. This ceremony was conducted by Stanley S. Ballard, Secretary for Local Sections, who subsequently addressed the meeting on the subject, "Optical Crystals."

The appropriateness of having a chapter of our Society in Chicago would surely not be doubted from the historical point of view. And there has been activity from time to time along the lines of forming a local optical group in Chicago. This finally came to a head in late 1947 and early 1948 when it was apparent to many that the local-section program of the Optical Society was moving ahead steadily. The leaders in this movement were Robert A. Woodson, a Consultant Optical Engineer in Chicago, Paul C. Foote, Chief Optical Engineer of the Bell and Howell Company, and Edward E. Bickel, Chief Optical Engineer of the Simpson Optical Manufacturing Company. The first organizing committee meeting was called for April 6, 1948, and a second meeting was held on April 26. Other members of the organizing committee were Russell A. Fisher of Northwestern University, Roscoe E. Harris of the University of Illinois' Navy Pier Branch, Robert E. Lewis of the Armour Research Foundation, Ralph H. Steinberg of Carnegie-Illinois Steel Company, Harris M. Sullivan, Assistant Director of Research of the Central Scientific Company, Frank S. Tomkins of the Argonne National Laboratory, and R. T. Van Niman of Motiograph, Inc. The first regular meeting of the newly formed Optical Society of Chicago was held on September 16, with the organizing committee in charge of affairs. Additional meetings were held on October 14 and November 16.

At the meeting of December 24, 1948, the following officers were elected: R. A. Woodson as President, P. C. Foote as Vice President and Program Chairman, Warren J. Smith of the Simpson Optical Manufacturing Company as Secretary, R. H. Steinberg as Treasurer, and the following Councillors: R. A. Fisher, George S. Monk of the University of Chicago, and R. E. Harris. Subsequent to R. E. Harris' untimely death in September, 1949, his place as a Councillor was taken by R. T. Van Niman. The chairman of the active Membership Committee was E. E. Bickel, and the chairman of the Committee on Arrangements was Albert M. Smith of the Bell and Howell Company. The charter membership of the Optical Society of Chicago, as of January 1, 1949, was sixty-five. The Society was incorporated in the state of Illinois on January 5, and a constitution and by-laws adopted. Regular meetings were held approximately monthly during 1949, and during the last month or two of that year consideration was given to applying for local section status in the Optical Society of America. A petition was drawn up, and was ratified by the membership at its meeting of January 25, 1950. This petition was submitted to the National Society, and was discussed at the meeting of the Board of Directors held in New York on March 8. Affirmative action was taken, and plans were made for the installation of the section at its regular May meeting.

At the time of its installation, the Chicago Section had a membership of over eighty, which included representatives of an unusually large proportion of the many scientific specialities that make up the broad field known as optics. Surely all members of the Optical Society of America join the national officers in wishing this youngest local section all success!

STANLEY S. BALLARD
*Secretary for Local Sections*